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THE
JOURNAL OF SOIL SCIENCE

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ROTHAMSTED EXPERIMENTAL STATION, HARPENDEN, HERTS.

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Correspondence on the subject-matter of the Journal should be addressed to G. V. Jacks, Esq., Commonwealth Bureau of Soil Science, Rothamsted Experimental Station, Harpenden, Herts., and all other correspondence to the Publisher:

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GILBERT WOODING ROBINSON, 1888–1950

(President of the British Society of Soil Science, 1949–50)

C. G. T. MORISON

(President, 1947–8)

An Appreciation delivered at the Summer Meeting of the Society, September 1950

I DO not suppose that any of us who were present at the joint meeting with the Society of Chemical Industry in the spring of 1950 could have imagined that we should be meeting here today without our President—but Fate has been unkind, and we are left to mourn his loss.

Our science has lost one of its leading figures, one indeed of the small band of pioneers, and the workers in the particular field in which he was most interested have lost a friend and a colleague. It is certain that we could not let this occasion go by—this occasion when he should have presided over our deliberations and when he should have enjoyed with us the field excursions—without making some reference to our loss, and to the sort of man we have lost.

He was to have given us today his Presidential Address. I am ignorant upon what particular aspect of pedology his discourse would have been, but I know that we should have been delighted not only by the matter of his address but also by the humour, and the slightly provocative manner in which it would have been delivered. It was not, however, to be, and he was taken from us with the powers of mind and body unimpaired—no bad way, it seems to us who were his near contemporaries, to pass on.

I shall be speaking more formally of our loss at the Annual General Meeting this evening, and my object this morning is to do something other than indicate what we have lost—to try and put before you what in my view our science has gained by the life and work of our late President.

In the development of science it is no easy task to assess the contribution made by any particular individual in the building of the whole structure. This is particularly difficult in the early stages of scientific history, and it must have been hard to value at its true worth the work of Dalton, Lavoisier, or even of Berzelius in the early days of modern chemistry. The passage of time makes the truth of a picture more certain and more easy of assessment. It is the same today in the early stages of the science of pedology—we are too close to the beginning to be able to evaluate with any degree of certainty the contribution made by a single individual.

I would therefore ask his friends to bear with me in my attempt to do so, if I seem to underrate certain aspects of his work or to lay undue stress upon others. I would also ask all of you here to remember that I am trying to do this today, not merely to give you some idea of his work, but also to pay a tribute to a friend and a scientific colleague.

It will prove impossible for me to discuss Robinson's work without referring from time to time to the man, for the nature of his work was determined by the character of the man. This is more true in the early

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stages of any branch of science than it becomes later on when research has been more canalized or even more stereotyped into well-marked and wellnigh watertight compartments.

I think that the life of any man, and especially of any scientific worker, may be divided into three portions or periods.

1. The acquisitive period in which experience is being gained by the individual, and knowledge is being acquired which will be put to use later on. It is, moreover, often true that it is during this period that a man's main line of work becomes established.
2. The distributive period in which the greater part of a man's active research is carried out, and which sees his greatest output of published work.
3. The contemplative period in which an attempt is made to consider the philosophical, using the term in its widest sense, implications of much of the work of the second period.

The second period may be indefinitely prolonged, and it may be split up on a time basis or on a subject basis into several components. While these periods in a man's active life are usually distinct, it is true that in the case of the more distinguished men of science, every aspect occurs in each period, and only the dominance of one aspect characterizes such particular periods. There is in particular a considerable carry-over from period 1 to periods 2 and 3, and I myself think it is true to say that the more distinguished the man the more difficult it is to determine the boundaries of a particular period.

Before trying to trace G. W. Robinson's contribution to pedology, let us consider for a moment the state of knowledge in soil matters when Robinson began his work.

How much he disliked the term 'soil science'! 'I do not propose', he says in one of his books, 'to use this barbaric term. I prefer to speak of my subject as pedology, a term respectably derived, like most philosophical terms, from the Greek.' In this country knowledge of soil conditions was still very largely bound up with agriculture and agricultural utilization. The dominant position of Rothamsted as a centre of soil work was unassailed, and the views of Gilbert and Warington modified by the researches of A. D. Hall and the young Russell still held the field. Hall had left Wye and had been at Rothamsted for some time, and comparatively recently he had been joined there by E. J. Russell.

The agricultural pundits Somerville and Middleton had followed each other at Cambridge and at the Ministry of Agriculture. Subsequently Somerville went to Oxford and T. B. Wood became professor at Cambridge, where he was head of the School of Agriculture when Robinson went to Caius College. The Agricultural Advisory Service was in its infancy, and was experiencing some of the teething troubles associated with those tender years. It was into this atmosphere that the young Robinson came when he decided in his Cambridge career to take agriculture.

He originally came from Wellington in Shropshire and had been at school in Wolverhampton, and went to Caius College, Cambridge, in 1907, with a variety of scholarships from the college, from the school,

and from the Salop C.C.—a fact which was very largely to determine his future. In 1909 he took a First Class in the first part of the Natural Science Tripos at Cambridge, and then for some reason or other he decided to sit for the Agricultural Diploma which he took in 1910. It is perhaps surprising that he adopted this course instead of taking Part II of the Tripos. His interests were entirely in the physical side and he had little use for biological studies.

In this connexion, L. F. Newman, who was at that time a demonstrator in the School of Agriculture, tells me that Robinson's name was entered by mistake for the optional subject physiology in the Diploma Examination. J. H. M. Marshall, who was examining, persuaded him to sit on the off-chance of picking up a few marks. During the oral examination Marshall tried with great kindness and consideration to find some subject in which a discussion was possible; being unsuccessful, he finally said, 'Well, Robinson, tell me something you do know.' This completed the débâcle and Robinson obtained precisely 0.

In 1910 and 1911 he was at Cambridge. There was at or about that time what might be called the first epidemic of soil-survey work in this country, beginning with the publishing of the *Soils of Dorset*, by Gilchrist and Luxmoore in 1907, and continuing with *Soils of Cambridge*, by Foreman in 1911, *Soils of Kent, Surrey and Sussex*, by Hall and Russell in 1911, *Soils and Agriculture of Norfolk*, by Newman in 1911, and *Soils of Nottingham*, by Goodwin.

About this time, probably in 1909 or 1910, at any rate while Robinson was still at Cambridge, the County Council of Shropshire offered to finance a survey of its area and suggested that its own county scholar should carry out the work. While he was at Cambridge Robinson had been engaged in work very different from soil survey. He took part in a team which was investigating the relative digestibility of white and wholemeal bread, as far as he was concerned, not on the biological but on the chemical and analytical side. In 1912 also he published a paper with Halnan on the probable error of pig-feeding trials.

When he decided to attempt the Shropshire survey he was handed over to Newman to learn the technique and to be initiated into the manner of field work as it was then understood. He worked side by side with Newman, each in his respective area, for two years. At that time they were very different in their outlook—Newman biologically minded and anxious to group soils on the basis of geology and ecology and field observation, Robinson the physical chemist believing that the solution of all survey problems lay in laboratory investigation of soil material. Although Robinson modified his view in later years and with more experience, up to the last he maintained that there was much in soil-survey work which could not be decided by observation alone, and that careful and selective laboratory investigation was needed to confirm and expand observational data. The survey of Shropshire was published by Shropshire County Council in 1912, and in that same year Robinson was appointed adviser in Agricultural Chemistry at Bangor.

It was while he was at Cambridge that Robinson developed his interest in languages and particularly in Welsh. He was not Welsh by descent

except to a very small extent, but he became completely immersed in this language study. So completely was he successful that in his later years he spoke Welsh so fluently that it is said that his accent was indistinguishable from that of a native-born speaker. His facility for languages was phenomenal: it was as a classical scholar that he went to Cambridge, and in later years he was at one time President of the North Wales branch of the Classical Association, and became a fluent speaker in French, Italian, and Spanish, and a moderate performer in German. It was this knowledge of Welsh that obtained for him the appointment at Bangor, where he remained the whole of the remainder of his life.

This move to Bangor, with its new surroundings and different interests, marked the close of the first period in Robinson's life. What picture of Robinson as he was at that time can we form now? He was evidently full of enthusiasm and keenness, immensely interested in Wales and things Welsh, eager to get on with his new work, in which he naturally felt that his knowledge of the Welsh language gave him a flying start. He was interested in soil-survey work as a result of his Shropshire effort, and he was also convinced that this kind of investigation would not only enable him to get acquainted with the physical nature of his area, but would also of necessity bring him into contact with many of the farmers. He was still, however, the physical chemist, and he still believed in the value of laboratory work as an essential part of any survey, and so he set himself to work to tackle the whole subject of mechanical analysis and dispersion, as being part of the analytical work necessary for the identification and interpretation of soil individuals as identified in the field. He regarded this, and I think we would agree with him, as one of the most fundamental determinations for survey purposes.

To the end of his life he was particularly sceptical about the value of field assessments of texture, although in many discussions I had with him on this subject in his later years he had come to think that for most survey purposes a modified analytical technique and a simpler grouping of particle size was adequate for most routine soil-survey purposes.

At the beginning of this second period of his active life we see him throwing himself with his characteristic exuberance into the attempt to familiarize himself with the district for which he was responsible as completely and as accurately as possible. What better way was there than in the preparation of soil maps? At the same time he was working to improve and shorten the methods of dealing with his specimens when they were in the laboratory.

Nine years after his arrival his Department was given University recognition, and he was made a University lecturer. In 1926 he was made a Professor, and in 1947–8 he acted as Vice-Principal of the College. During the whole of his time at Bangor he combined the offices of adviser, research worker, and teacher with singular success, and there are few soil workers in this country or overseas who have not at one time or another come under his influence, and who do not owe much to his inspiration and example.

In Wales his survey efforts began, as I have said, at once, and in 1917 he published his first paper on the Palæozoic soils of Wales to be followed

in 1919 by a further paper on the same subject in collaboration with Hill. It is, moreover, worth remembering that in 1915 a paper by him and Lloyd on the probable error of sampling in soil surveys appeared—a subject which might well have been borne in mind in later surveys. In the meantime, the laboratory work was making progress, and a preliminary paper on changes in water viscosity at varying temperatures was published in 1915.

I think that the war years 1914–18 were mainly occupied by the soil surveys to which I have already referred, and by his advisory work, as it was not until 1922 that his paper on the results of his mechanical-analysis work appeared. This work, which was purely physical in conception, was contemporaneous with that of Krauss in Germany, and was an elegant device for shortening the sedimentation method of mechanical analysis then in vogue.

He was now satisfied with the method of analysis, though in certain cases difficulties remained, and in the same year a paper on the mechanical analysis of humus soils was published. Though he was now content with the method, he was not satisfied with the usual statement of results, and in 1924 he published a paper on 'The Form of Mechanical Composition Curves of Soils and other Granular Substances', showing the well-known forms of curves when summation percentages in a mechanical analysis are plotted against the logarithm of the settling velocities of each group.

At about this time the International Society of Soil Science met in Rome and decided to undertake extended co-operative work in these new methods to test different methods of dispersion and to compare the pipette method of sampling with the older complete sedimentation methods. Robinson undertook to organize the British contribution and acted as recorder and reporter of the work, and it was out of this co-operative work that the international method of mechanical analysis was developed. This was the beginning of his association with Commission I, the soil-physics commission of the International Society—an association which he maintained until the outbreak of war in 1939.

I shall have more to say later on about his association with the International Society. It was at the meeting in Rome in 1924 that I first got to know him well. He was always very much at home at international meetings, where his great facility in languages made him doubly welcome. In Rome he was, of course, particularly happy, not only because of his interest in the language and culture of ancient Rome, but also because he was very much of a churchman, and, as such, could not fail to be impressed and influenced by the medieval and ecclesiastical city.

With the 1914–18 war and the influence of the Russian school of pedology, he was to see soil-survey methods change almost completely with an ever-increasing emphasis on observational and field records. Robinson readily accepted these changes, and incorporated them into his work in Wales, and his welcome for the ideas of soil-profile descriptions was characteristically whole-hearted. At the same time he held tenaciously to the view that none of this was really worth while, none of it could give a complete interpretation of any soil profile unless it was

confirmed and supported by suitable analytical data. On page 509 of the third edition of his book, *Soils*, published in 1949, he writes: 'The identity of a soil profile must rest ultimately in some securer basis than qualitative and personal judgement.'

After the completion of his work on mechanical analysis he turned his attention to the organic component of a soil profile. In field-survey methods the content of intimate humus was estimated on colour alone. This he felt to be unsatisfactory for a variety of reasons, but principally, I think, because all humus is not the same colour, and he set to work to devise a method which was at the same time accurate and rapid, and capable of routine development.

In 1925 he and Jones produced a short paper on the degree of humification of soil organic matter making use of hydrogen peroxide, and in 1929 he, McLean, and Rice Williams brought out a much more substantial paper on the determination of organic carbon in soil. I think that he felt that this method gave him what he wanted, though he appreciated the difficulty in translating his carbon figures into humus.

Having thus devised means of determining size distribution with accuracy and reasonable speed, and the carbon content of a soil which was convertible into organic matter, he next turned to the nature of the clay fraction. He communicated a note to *Nature* in 1928 on the nature of clay and its significance in the weathering cycle. In 1930 he published a paper on the development of the soil profile in North Wales as illustrated by the character of the clay fraction. It was mainly on the basis of this work that he considered that very many soils in North Wales showed truncated profiles, and that the surface soil of the present time was in reality the B horizon of a developed podzol formed with a different vegetation association under rather different climatic conditions. He had, then, by these three distinct pieces of work provided means for giving precision to profile descriptions as regards particle size, organic-matter content, and the nature of the clay fraction associated with each layer.

During this time he was, of course, carrying out his duties as an advisory officer, and doing his share of teaching. With his work as advisory officer went the newer surveys of North Wales soils of which progress reports were published in the *Welsh Journal of Agriculture* in 1928 and in 1930, and an article on the soils of Wales in the *Empire Journal of Experimental Agriculture* in 1934.

Until the year 1926, from the time of the earlier surveys and in particular of Hall and Russell's survey of Kent, Surrey, and Sussex, soil survey in this country had been carried out mainly by advisory chemists, in their own areas and by their own methods, and no attempt had been made except by informal discussion to obtain either uniformity of method or a comparable method of presentation by results.

In 1926 Sir Thomas Middleton had become convinced that this meant waste of effort and loss of information, and that some means of correlation was not only desirable but essential. At a meeting of advisory chemists and others, held at Harper Adams Agricultural College, it was decided to attempt to bring about this co-ordination. A decision was taken at that meeting to form what was in effect a committee of the

advisory chemists which should meet each year, once in the field and once at the Ministry of Agriculture. The objects of these meetings were to attempt to unify the various methods then employed, to formulate future policy, and to suggest improvements in field technique and in methods of mapping. Robinson was elected chairman of this gathering, and Morley Davies secretary. Gradually, owing to Robinson's patience, good humour, and tact, and Morley Davies's unstinted help, unification of ideas and of method was achieved. From that time, in fact if not in theory, soil survey became a national endeavour.

Robinson was in many ways an ideal chairman—he knew what he wanted, he never came to a meeting without knowing his brief from beginning to end, he never curtailed discussion, but in the end he usually got what he wanted. It was not only in soil-survey matters that this ability of his was to be of great value. These meetings of soil surveyors led to the formation of the soil correlation committee, of which he was also chairman.

In 1939 he was made Director of the Soil Survey of England and Wales, an office which the war prevented him from developing and which he held until 1946. In that year Dr. Muir was appointed to succeed him and the headquarters of the survey were moved to Rothamsted.

I have mentioned earlier that Robinson took much interest in the meetings of the International Society of Soil Science and co-operated in the work of that body from the time of its reconstitution at the Rome meeting in 1924 until it became moribund with the outbreak of war in 1939. As already stated, he acted as recorder and collector of data for the British Isles in connexion with the co-operative work on mechanical analysis, and he was present at the First International Congress in the U.S.A. in 1925; he was not present at the Second Congress which was held in Leningrad in 1930, but subsequently he was elected President of the First Commission, i.e. the soil-physics commission, which office he held at the Third Congress in Oxford in 1935. He was also Commission President at the meeting of the First Commission at Versailles in 1934, where he spoke on dispersion methods, and at Bangor in 1939, immediately prior to the outbreak of the second war.

He was, as I have said, singularly happy in these international contacts, not only because he was a born linguist and could talk with most Europeans in their own languages, but also because he was unlike many scientific workers in one respect, in that he was keenly interested in people; in fact it sometimes seemed to me that he was more interested in the people talking than in what they were saying.

In 1932 there appeared his book *Soils—their Origin, Constitution, and Classification*, of which the third edition appeared last year. This book must be familiar to everyone, to every student, to every teacher, and research worker in this country. It is unique as the first English text-book to be published on pedology, and I think that for many years to come it will remain a standard text-book on this subject. It is in some respects an easy book to criticize, as perhaps any book on the same subject may well be, and its omissions and its weaknesses are at times surprising. In spite of these, I believe that it will be a long time before its usefulness ceases.

About 1936 Robinson began to pass from the active period of his life to the contemplative period in which he was to sit back and consider the ultimate value of much that he himself and others had done. His other book *Mother Earth* has in it the beginning of those thoughts. It is an odd book, one which never could be popular, but which none the less gives us a very faithful picture of the man. Most people here will no doubt be familiar with it; it is written in the form of letters to Sir R. G. Stapledon, and begins with a quotation from St. Francis of Assisi and closes with a chapter 'Concluding Reflections' from which I quote.

> The idea of perfection is a legacy of the past, it includes the Greco-Roman literary and artistic tradition; it includes Christian morality, and imposes on us beauty, truth, justice and moral perfection as the aims of life. Contrasted with this is the ideal of human power over nature; the ideal of material welfare as the highest good; the ideal influenced by crude ideas of evolution that lures on mankind with the belief in the inevitability of progress. The ideal of perfection implies the recognition of appointed limits to all human activity. The ideal of power knows no such limits, but drives man relentlessly along a path no longer of his own choosing.

Who but Robinson, and Robinson in the contemplative period of his life, could have introduced these words into a book on soils? The time may come when this book will be regarded as one of a small number of scientific curiosities—characteristic of an age when the road was obscure and the goal uncertain.

After the war the contemplative period again reasserted itself, and was made manifest by a talk he gave to the Conference on Tropical Soils held at Rothamsted in 1948, and by the paper which has been published in the second number of the *Journal of Soil Science*. This latter is, I think, most characteristic of the man, of the contemplative period of his life, not so much for the matter of his contemplation as the manner of it. As in *Mother Earth*, he is trying to relate his own scientific experiences to a wider field and to realize something of the ultimate meaning of his work and of that of others.

> Now whether the universal podzol can be taken in a Realist sense and be conceived as existing apart from its observed characteristics or whether it is merely a complex of observed and observable qualities or relations is the central problem of the discussion. The writer ventures to think, perhaps mistakenly, that the idea of a podzol, if it is a universal, is a constructed universal, the complex of characteristics that make up the concept can only be a creation of the pedologist; yet not an entirely arbitrary creation, for a certain ensemble of properties is given, and does with certain variations occur in nature.

No contemporary pedologist other than Robinson could have written these words.

In this short and general survey of his work I have obviously not mentioned everything which he did nor all that he published. There were other papers in the same or kindred subjects in journals and other publications, and I have selected what seemed to me the most important and the most characteristic.

At this distance, so close to the living man, it is almost impertinent to attempt a valuation of the permanent worth of his work. The only thing that I can do is to state my own opinion, though it is more than likely if

I were able to look back on his work from another 20 years in the future, I might take a different view. Of his written work, that on mechanical analysis and its interpretation seems to me to be the most important thing which he did, considered, as it must be considered, against the background of soil survey. As I have repeatedly said, he was opposed to the purely observational approach to survey problems, and he felt that in one direction at least his work had given the precision he thought necessary. That work and his book remain, in my view, his most substantial written contribution to the science of pedology.

Much more, however, will remain of his work that was not written. Most of those who have done or are doing work of this kind in various parts of the world came under his influence at one time or another. It would be difficult to find anyone in this country who had such a wide personal effect upon the subject as had Robinson. This effect was obtained much more by personal contact than by the written word. His successful work for the soil-survey conference in this country, his work for the International Society of Soil Science, his work during the war, and his work in connexion with this Society were largely brought about by personal contacts. It is because of those contacts that his influence will remain, and even when the memory of his personal qualities has faded, and the number of those who knew him has grown less, the effect of his personality will still persist, and will make the science of pedology the richer for his being.

It is not my purpose to say more about his other activities and distinctions—his presidency of the North Wales branch of the Classical Association, his membership of the Dialectical Society, his work as Justice of the Peace, his Fellowship of the Royal Society (the first pedologist to be so honoured)—you will find these in the obituary notice contributed to *Nature* by Sir John Russell. Sir John there says of him: 'he was never hurried, never tired, he was acceptable everywhere and was trusted and esteemed by all'.

He came from Shropshire; he was very much attached to that county and to Wales the country of his adoption, and to the Welsh Marches. He remembered to the last the fields which he sampled in his first survey when he was only 23.

Robinson dedicated his book to Curtis Fletcher Marbut, who directed the soil survey of America for 25 years and who was a close friend of his and for whom he had the greatest admiration. He uses in his dedication the following words: 'The loftiness of his scientific ideals, the nobility of his character, and the kindliness of his disposition won the admiration and affection of all who knew him. His death was untimely and his loss irreparable.' I can think of no better epitaph for Robinson himself than these his own words.

A SOIL SURVEY ON WARPLAND IN YORKSHIRE

W. R. HEATHCOTE*

IN the lower valleys of the Ouse and Trent and bordering the Humber there is a considerable area of low-lying riverside land known locally as the 'warpland'. The term warp refers to the sediment carried by the river whether it is still in suspension, deposited in the channel as a mud bank, or left as a fertile deposit after flooding on land adjacent to the river.

Soils formed on this deposit are very suitable for investigations on the speed and intensity of profile development, as the principal variables (Jenny, 1941) are the drainage conditions prevailing at the site and in the soil, and the length of time which has elapsed since the parent material was deposited. Other factors such as topography, climate, and parent material are constant. These soils also afford an opportunity to investigate the development of profiles under conditions of impeded drainage, and this in turn allows some conclusions to be drawn as to the reasons for success or failure of warping, and the resulting effect on agricultural practice.

Warp and Warping Practice

There is an old and still commonly held belief that the apparent undue amount of sediment or warp in the Ouse, Trent, and Humber is due to the inwash of material from the Holderness coast which is being actively eroded by the sea, but this at best could only apply to the Humber, and in the Ouse and Trent, as in any other river, the sediment is probably derived from the river basin. As many of the geological formations occurring in the basin also occur on the coast, comparative mineralogical analysis would not help in deciding the source of the deposits, but the old theory has been shown to be inadequate by W. H. Wheeler (1901), from whose writings the facts in the following paragraphs have been taken, although Wheeler later modified his extreme views somewhat (cf. Sheppard, 1912).

The tide only flows for 3 hours and ebbs for 9, and although the effect of the tide is felt as far up the river as Naburn near York, and warp occurs at Cawood, the water is normally fresh at Goole. There is a zone of maximum accumulation of warp in the Ouse and the Humber that oscillates with the tides and lies between Goole and Brough. As the tide flows 6 hours at Spurn at an average of 4 miles per hour, solids in the river there could only reach 20 to 30 miles up river, and at the ebb they would still be 20 miles below the zone of maximum accumulation, while at the beginning of the next flood they would be well out in the North Sea.

* This study was carried out when the writer was a member of the Soil Survey of England and Wales and has been used, in part, in a thesis submitted for the degree of M.Sc. at the University of Durham. The article has been edited and supplemented with further analytical data by Dr. A. Muir.

The river itself affords the most convincing arguments that there is little inwash into it from the coast. At Whitton, near the junction of the Trent and Ouse, the water carries 264 grains/gallon (3·76 g./l.) of salts in

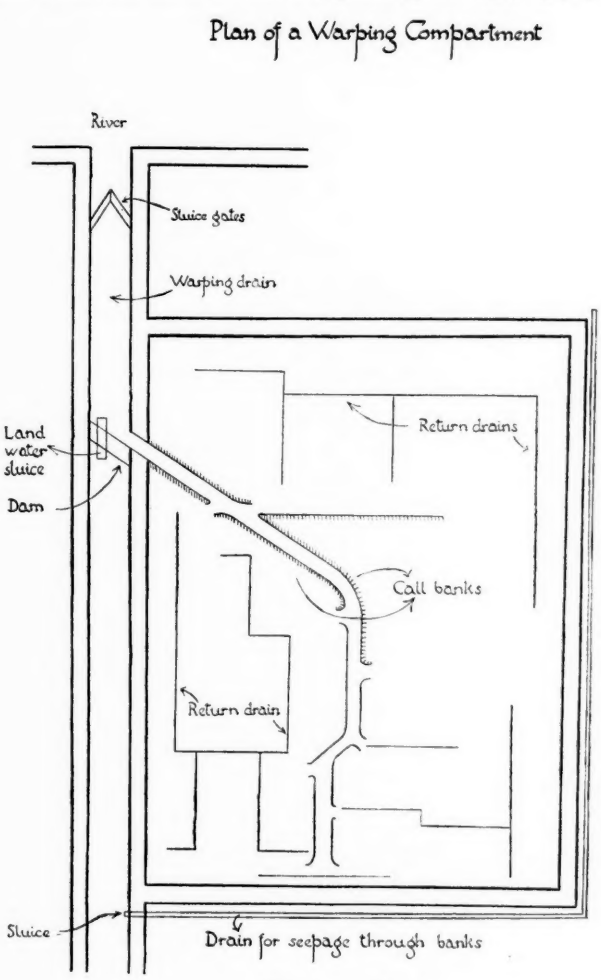

FIG. 1.

solution and 5·4 grains/gallon (0·077 g./l.) of solids in suspension. This amount of salts in solution is only 11 per cent. of the amount carried by the flood-tide at Spurn. Since matter is more easily transported in solution than in suspension, it is unlikely that the flood-tide at Whitton could carry 450 per cent. more solid matter in suspension than it did at Spurn.

Wheeler does not explain, however, why a zone of maximum

accumulation should occur, but it is not difficult to find an explanation. Deposition occurs where the régime of the river finally gives place to that of the tidal estuary. In the estuary there are strongly flowing tides varying from 15 to 22 ft. These tides so check the speed of the river that much of its load is deposited. This check is accentuated or, more truly, the intensity of the flood-tide is increased, thus augmenting the check, by the shape of the river at this point. In a distance of 8 miles (14,700 yds.) from Ferriby Sluice to Trent Falls the river narrows from $2\frac{2}{3}$ miles (3,640 yds.) to less than two-thirds of a mile (1,050 yds.). Thus the immense flood of the tidal water of the wide Humber is suddenly confined to the narrow Ouse, making the flood-tide there very intense although only of short duration. This flood not only checks the river, making it deposit its load, but it also scours the bed and banks of the river, bringing into suspension again the deposit left by previous tides. Dry summer months are most favoured for warping because then the flow of the river being at a minimum, the tide, driving into the suddenly narrowing channel, has a maximum scouring effect on the bed and banks so that a maximum amount of material is brought into suspension and therefore on to the land.

Warp is typified by a high content of fine particles in contrast to the coarse sandy alluvium found higher up the stream. The tidal check to the flow of the river is so great that even the finest particles are deposited. This check, however, is soon minimized by the normal flow of the river, so that warp does not occur to the highest point of tidal flow.

By 1750 the technique of warping had been established, and from then until the present day poor land within a reasonable distance of the river has been improved by warping. However good the technique may be, initial and ultimate success depends entirely upon three essential conditions supplied by nature. The first of these is the tidal régime of the river which gives a sudden high and rapid rise in the river level with a long ebb. The second is the heavy load of sediment brought down from the extensive drainage basin of the Ouse, while the third is a large area of riverside land which lies between the levels of high and low tide.

Warping is carried out as follows: the chosen area is strongly embanked (Creyke, 1844) with banks having a slope on each side of 15–18 in. for every foot in height, and where they need to be particularly strong the centres are puddled. The area inside the main embankment is divided according to micro-relief by smaller 'call banks' (Fig. 1) so that the inrushing water is spread as quickly and as evenly as possible over the whole area, thus giving a uniform deposit. Flood-tide water is let into the compartment through a large open ditch called the warping drain, which has sluice-gates at the outfall into the river, and these may be opened and closed at will. The inrushing current must not be too strong and must be controlled, or sandy patches are formed and the resulting warp is uneven in texture and the surface is not level. For success it is essential that the water be let on and completely off again every time the compartment is flooded, hence the multiplicity of small return drains to clear away the last water which otherwise would lie about in puddles in the lower parts. The highest tides can only be used for warping at some

distance from the river, so that by the time it enters the compartment the rush of water has slowed down somewhat and does not damage the banks. The depth and width of the drain varies with the length, but the aim is always to have as free a flow of water as possible in order to minimize silting-up. To further this aim spring tides are used as much as possible so that the strong ebb has a good scouring effect on the drain.

When warping has been completed the land is left to dry until it can be walked on with the aid of mud pattens or mud boards. Italian rye grass, or a grass mixture, or a grass and oat mixture, is then sown with a fiddle drill (Seton, 1931). When grown this cover helps to dry out the warp further, and the stock which are put to graze on it aid consolidation of the surface and help to fill in the cracks that make a close mosaic over the surface as it dries out. When consolidation is deemed to be sufficiently advanced the land may be divided into fields, drained, and put under the normal crop rotation. When saltings are embanked from the river they are generally supporting a grass vegetation which has been regularly grazed in the summer for some years. Hence a minimum of consolidation and drying out is necessary and the land is more easily brought into regular arable cultivation.

When land is low-lying, and especially when it is at some distance from the river, it can only be warped every second or fourth tide as there is but a short period at the ebb when water can run off the land. Therefore a long period must elapse before it may be flooded again.

Conditions in the river are not always suitable for warping and none is done during frosts, high winds, and when there are land floods in the river. Frosts can damage wet embankments and block sluices with ice; high winds, especially from the east, can cause unexpectedly high tides which may be disastrous to weak embankments or to those designed only for smaller tides. Winds may also cause wave damage to compartment banks. Land floods in the river result in a very small deposit of warp per tide and may even cause active erosion of the deposit already in the compartment. Most warp is deposited during fine dry weather and the spring tides at the equinoxes are considered the best (Thornton and Herapath, 1850). No area should be finished in June or July when the river is very low, because with the increased salinity undesirable salts are left in the surface. Any such area although built up mainly in the summer should be finished later in the autumn so that the surface is practically salt-free. This allows the first cover crops to be grown and also sufficient time elapses before ploughing for any salt present to be leached to a safe depth.

The rate of accumulation (Thornton and Herapath, 1850) varies considerably. Where there is a good depth of water at each tide, from 2 to 3 ft. of warp may be laid down in a year, but on higher land it may take 2 to 4 years for the same depth to accumulate. When the river is suitable for warping it contains about 4 tons of warp per foot of water per acre which, with a depth of 3 to 4 ft. of water, means about one-tenth of an inch deposit per tide. From April to November with 3 ft. of water at spring tides and 2 ft. at neap tides about 2,300 tons/acre of warp will be deposited, or a thickness of about 18 in.

Parent Material and the Effect of Underlying Formations

A soil survey was carried out on land built up in the above way either naturally or artificially and all the soil series found have been developed entirely on this deposit.

Warp is a highly calcareous and micaceous fluviatile or alluvial deposit which may be of a fine sandy or of a silty nature, and there is a conspicuous lack of coarse sand.

The texture of warp is determined by the speed of movement of the water from which it is deposited. At such places as Sand Hall, Saltmarshe, or Broomfleet Island, where the tidal flood had unrestricted flow, the natural deposit is mainly sand. At Blacktoft or Ellerker Sands, where the land has been artificially warped, and the water has been still sufficiently long for some of the finer particles to settle, the deposit contains a much higher proportion of silt and some clay. Even in such areas, however, in the runs between the 'call banks' where the water has been moving faster the deposit is again of a fine sandy nature.

There are exceptions to these generalities, some of the natural warp at Ricall being of the heavier type although deposited from moving water and some of the artificial warp south of the river in Goole Marshland being very light.

In most places the warp is more than 3 ft. 6 in. thick, but in a few small areas the underlying formations are within reach of a 42-in. auger. They are carr peat, lacustrine clay, post-glacial sand, and fluviatile sand. Peat is supposed to maintain under drainage, but all the series occur in places on peat, including some of the worst drained warp in Hotham Carrs. Lacustrine clay appears to give rise to a heavier soil, as wherever there is clay within 42 in. of the surface the soil is heavy, but heavy soils also occur where there is sand at considerable depth (7 ft. or more). In other places, whether the warp is thin or thick, the sands appear to give rise to a lighter textured and better drained soil. It may be said that the underlying formations only play a minor role in profile development.

The Soil Series—Classification and Morphology

Virgin soils are almost non-existent on the warpland. The saltings—the area outside the levee having a grass cover but flooded by spring tides—are immature soils although uncultivated, while all other warp soils have been cultivated at some time or other and, except on particular soil series, it is difficult to say how the soil would have developed under natural conditions. However, the soils have been classified according to their present characteristics under more or less intensive cultivation and fall into the following groups:

Brown Earth with gleyed B and/or C horizons.
Surface Water Gleys—Calcareous.
Ground Water Gleys—Non-calcareous.

As local opinion is far from unanimous as to the source and nature of warp and even as to where some of the older warp soils occur (Sheahan and Whellan, 1855), and there are no maps* showing in detail the dis-

* The maps were consulted in Hull City Library. A selection has been printed by Sheppard (1912).

tribution of warped land, the area chosen for detailed survey included land which had been warped for the present tenant and the history of which was known. This land provided a sure basis from which to begin mapping and from which to build up details of profile development in warp soils and to sort out the relative importance of the various factors involved in that development.

There are four main series, Saltmarshe, Blacktoft, Wallingfen, and Gowthorpe. A fifth series of very small extent is the Staddlethorpe.

The Saltmarshe Series. The Saltmarshe Series consists of a warm brown silty clay loam. It is a deep soil (over $3\frac{1}{2}$ ft.) with a poorly developed profile though markedly laminated, and it is highly calcareous. It belongs to the group of Brown Earths with imperfect drainage or weakly gleyed B and C horizons. The following profile illustrates the morphology.

*Saltmarshe Clay Loam** [*Fine Sandy Silty Loam*] (*No.* 6)

Locality: White House Farm, Sunk Island. Elevation: 13 ft. above O.D. Date of deposition: *c.* 1650.

Description:

A	0–13 in.	Warm brown (darker in top 9 in.). Silty clay loam. Crumb structure. Friable. Calcareous.
B_1	13–19 in.	Warm brown, pale buff laminae. Silty clay loam. Laminated. Friable.
B_2	19–27 in.	Warm brown, pale buff laminae, widely scattered iron staining. Clay loam. Slightly laminated. Fairly compact. Calcareous.
C	Below 27 in.	Paler brown, strongly marked buff laminae. Sandy loam. Strongly laminated, fairly thick laminae about $\frac{1}{8}$ in., and clearly marked. Friable. Calcareous.

Although this profile is from the oldest part of Sunk Island it still contains much disseminated carbonate (*c.* 8 per cent. $CaCO_3$). The series as a whole shows the least profile development and must have changed very little after deposition as the chief differences between the horizons are only of colour, and there has been no development of structure except in the surface. The laminations formed during deposition are very noticeable, being bands of silt varying in thickness up to one-quarter of an inch, separated by a very thin layer of fine or very fine sand, which carries the calcium carbonate always present in the profile. The fine sand is deposited soon after the water is let on to the land and the silt follows as the water becomes still. In some profiles laminae up to half an inch have been observed, but these are unusual.

The Blacktoft Series. Soils of the Blacktoft Series belong to the same group but they are heavier in texture than those of the Saltmarshe Series. They are dark yet warm brown fine sandy silty heavy loams, and the depth of the profile is very variable. The following profile illustrates this series.

Blacktoft Silty Clay [*Silty Clay Loam*] (*No.* 17)

Locality: Elleker Sands, Brough. Elevation: 12 ft. above O.D. Date of deposition: 1800–30.

Description:

A	0–9 in.	Dark greyish-brown. Very fine sandy silty clay. Mellow. Conchoidal nutty structure. Slightly calcareous.

* The soil and texture names are given in the current Soil Survey grouping. Mr. Heathcote's original type names are given in square brackets.—A.M.

B	9–32 in.	Warm brown, rust and pale grey mottled. Very fine sandy silty clay. Compact. Columnar prismatic structure, somewhat greyer appearance on the interfaces of the structural elements. Faint remains of lamination. Some calcium carbonate.
C	Below 32 in.	Warm brown, rust, and pale grey mottled with buff-coloured fine sandy bands at fairly widely spaced intervals. Silty clay loam. Compact. Laminated. Much calcium carbonate.

The soils are calcareous, though not so markedly so as the Saltmarshe Series. Although the laminations of deposition may sometimes be clearly seen in some of the old as well as in some of the youngest profiles, there is no division of fine sand and silt into separate laminae as in the Saltmarshe Series. The laminations are generally completely masked by a well-marked structure which has developed later and forms the greatest difference between the horizons. On a weathered ploughed surface a very typical starchy structure develops and even under grass the conchoidal nature of the small elements is not completely lost. In the deeper horizons long vertical prisms and wide permanent vertical fissures are developed. It is interesting to note that where this series overlies lacustrine clay the structural elements and vertical fissures of the warp coincide with the original ones in the clay. In the heaviest soils of this series there is also a slight grey varnishing on the interfaces of the structural elements showing incipient gley tendencies which would no doubt develop quickly should the drainage become impeded.

Staddlethorpe Series. The Staddlethorpe Series belongs to the group of Brown Earths with gleyed B and C horizons, and is intermediate in texture between the Blacktoft and the Saltmarshe Series. It only appears where thin (less than 3 ft.) artificial warp overlies sandy lacustrine deposits or riverine sand and is of very small extent.

The Wallingfen Series. In this series drainage is impeded in the surface and the soils are classed as Surface Water Gley Soils. The profile is distinctive and is characterized by a grey-brown rust-mottled heavy loam surface from 4 to 12 in. deep, followed by a conspicuous and heavier textured blue-grey gley layer of varying depth, which passes sharply into pinkish-brown silty heavy loam with pale grey streaks. Although the thickness of each horizon may vary somewhat the sequence is always the same. The colours are very definite and the change of colour from one horizon to the next is very sharp. The gley horizon is the outstanding feature of the Wallingfen Series not only in colour but also in texture and structure. This series can best be illustrated by a profile from one of the oldest warp areas. The site is on the northern outskirts of the city of Hull.

Wallingfen Clay [*Clay Loam*] (*No.* 20)

Locality: Inglemire Lane, Cottingham, Hull. Elevation: 7 ft. above O.D. Date of deposition: before 1250.

Description:

A	0–4 in.	Grey-brown, rust-mottled clay. Loose. Hard crumb structure.
G_1	4–9 in.	Darker, blue-grey, brown and yellow streaked clay. Indurated. Columnar prismatic structural elements. Wide continuous vertical fissures beginning in the A horizon and ending in the G_3 horizon.

G_2	9–20 in.	Warm pinkish-brown, pale blue-grey and rust-mottled clay. Compact. Well developed and difficult to break columnar prismatic structural elements, often continuous from G_1.
G_3	20–26 in.	Warm brown clay, paler blue-grey mottled, large ochreous blotches. Cloddy structure poorly developed and easily broken. Tenacious.
C	Below 26 in.	Blue-grey, pinkish-brown and rust equally closely mottled clay. Structureless. Plastic.

Carbonates are completely leached from this soil, but a trace occurs in the C horizon.

While the surface may be of a medium or heavy loam texture the gleyed layer is always clay which gives place gradually to a somewhat lighter texture again in the lower layers. This striking change in texture occurs wherever there is gleying, and is particularly noticeable in the Gowthorpe Series. Structural changes are equally as striking. In the gley layer there are well-developed and mechanically strong pyramidal or columnar-prismatic structural elements separated by well-marked vertical fissures. By contrast, in the lower horizons there is only a weak cloddy structure which has not developed sufficiently to mask the laminations of deposition.

In the younger soils of this series the leaching out of carbonate does not extend below the A horizon and even here there are usually small amounts. In these cases there is usually a marked increase in carbonate in about the G_3 horizon and occasionally small secondary concretions occur at about 3 ft.

Drainage in this soil series may be divided into two parts. There is an excess of surface water (*v. infra*, p. 11) which percolates to a varying depth and there forms a zone of permanent waterlogging, producing the grey colour indicative of anaerobic or reducing conditions. This grey layer terminates in a zone of temporary waterlogging where periods of aerobic conditions have resulted in an accumulation of orange-rust and yellow-brown colours. Below this the soil is subject to rises of the ground water but rarely, for the permanent water-table is low. While it is generally below $7\frac{1}{2}$ ft., in two cases it was observed within 5 ft. of the surface.

While the movement of water from above and on rare occasions from below may have led to the accumulation of finer particles at their limit of travel in the gley layer, increased rate of weathering is more likely to have been responsible for the heavier texture. It is noticeable that wherever there is gleying the texture is markedly heavier; the most strongly gleyed profile in the Gowthorpe Series is much heavier than any of the other heavy, but better drained, profiles in the Blacktoft Series.

An impermeable layer beneath the surface has been noted by Hissink (1938) in some of the older Dutch polders on marine clay; he calls it a 'ploughsole'. It is possible that cultivation initiated the compact layer in the Wallingfen Series and suitable surface-water conditions developed it into a gley horizon.

The Gowthorpe Series. Soils in the Gowthorpe Series are classed as Ground Water Gley soils. The surface soil is dark and where undisturbed for a long time a humose layer has developed. Apart from this,

the horizons are indistinct and merge into each other. Colours throughout are dominantly grey and change little with depth. All traces have disappeared of the original laminar structure, which has given place to pyramidal or columnar-prismatic structural elements separated by wide and permanent vertical fissures. Calcium carbonate has been completely leached from the profile. The following profile illustrates this series.

Gowthorpe Silt Clay (*No.* 18)

Locality: North Farm, Hotham Carrs. Elevation: 8 ft. above O.D. Date of deposition: 1800–20.

Description:

A	0–7 in.	Dark grey very slightly rust-mottled silty clay. Friable. Small cloddy structure. Narrow discontinuous fissures. No calcium carbonate.
G_1 and G_2	7–24 in.	Blue-grey clay, marbled shades of rust. Local concentration of rust in nodules and heavy streaks. Tenacious. Columnar prismatic structure. Wide and long vertical fissures. No calcium carbonate.
	Below 24 in.	Carr peat of great thickness.

This profile, formed in warp overlying carr peat, is very similar to the meadow bog soil (Joffe, 1936) which is found with a cover of the coarser grasses and rushes where seasonal flooding, or waterlogging to the surface, is common and the permanent water-table is always near the surface. It is probable that if the drainage of the site became poorer it would nullify the effect of the deposition of the warp so that carr peat would once again become the surface soil, and the cycle would be complete.

Saltings and New Warp. Morphologically the saltings can be considered as being nearest the Saltmarshe Series and belonging to the group of Brown Earths. The following profile is typical.

Blacktoft Saltings (*No.* 16)

Elevation 20 ft. Date of deposition: very recent and still continuing.

Description:

A	0–12 in.	Dark brown. Fine sandy silty heavy loam. Friable. Structureless. Calcium carbonate present.
B	12–24 in.	Brown. Silty heavy loam. Friable. Faintly laminated. Much calcium carbonate.
C	Below 24 in.	Pinkish rust-brown, some pale grey mottling. Fine sandy medium loam. Friable. Faintly laminated. Much calcium carbonate.

This profile was exposed in the river bank outside the levee in the saltings which are flooded by only the highest spring tides. The vegetation is coarse grasses and herbs of a type peculiar to those areas open to flooding by brackish water. Although water began to seep in at 22 in. and flowed in much more quickly at 30 in., the colours are not those of a gley profile, nor do the analytical figures indicate that it is such.

Series: New warp—undifferentiated

Profile Number: 21. Locality: Blacktoft Clough, Blacktoft. Genetic group: Undifferentiated alluvium. Elevation: 3–7 feet below high-water mark of ordinary tides. Date of deposition: Very recent, still continuing.

Description:

	0–6 in.	Brown. Fine sandy silty medium loam. Much calcium carbonate.

The new warp (No. 21) was sampled at the mouth of Blacktoft Clough at an elevation of 3–7 ft. below the high-water mark of ordinary tides. Here eddies are formed in the current and the deposit is therefore more like the warp deposited in the field than that found on the open river bank, where, with a freely flowing current, it is more sandy.

Interrelationships. When considering the interrelationship of these series it is essential to remember that the mud (Profile No. 21) may be taken as typical of warp when it is first deposited on the land and before subaerial weathering is initiated, while the Saltings profile (No. 16) is the basic 'immature' profile from which all the others have developed. The series as described may be taken as representing the 'mature' soils for the given conditions of drainage and texture of parent material. It is possible that with changes in drainage conditions a gley profile may develop after some years on what was a well-established Brown Earth, but wherever there is a small excess of surface water or a high water-table the essential features of a gley profile are developed almost immediately and progress is rapid. That profile development can be extremely rapid under suitable conditions is shown by one of the profiles in the Gowthorpe Series which showed, in morphological and chemical characteristics, a well-developed ground-water gley profile only 20 years after deposition. Each series may be considered the 'mature' soil for its own conditions and not a phase in the transition to some different soil of greater 'maturity'.

Series Distribution and Factors in Profile Development

Of the three main variables in profile development, climate, parent material, and site characteristics or environment, the macro-climate throughout the warpland is for all practical purposes the same and while the parent material is of two types, fine sandy loam and silt clay, textural variation is of secondary importance in profile development, for the Wallingfen Series, occurs on both lighter and heavier parent materials and indeed most often on the former. In contrast, however, where either natural or artificial drainage conditions within the profile are good, the texture of the parent material plays a major role and determines whether Blacktoft or Saltmarshe Series shall occur. Of the site characteristics, drainage is the most important and is, in warp soils at least, the determining factor in profile development.

There are two main types of site drainage here. Where the permanent water-table is low and only rises very occasionally to within 2 or 3 ft. of the surface the Saltmarshe and Blacktoft Series develop.

Where, despite the raising of the land surface by warping, the water-table is always near to the surface and at certain times of the year at the surface, the Gowthorpe Series occurs.

Superimposed upon the first drainage type is a third in which excess surface water, unconnected with the ground water, results in a zone of water-logging close to the surface. This excess surface water may be due to inattention to detail in draining after warping or to an embarrassment of the surface drainage system by run-off from adjoining higher land, or to a combination of both. Under these circumstances the Wallingfen

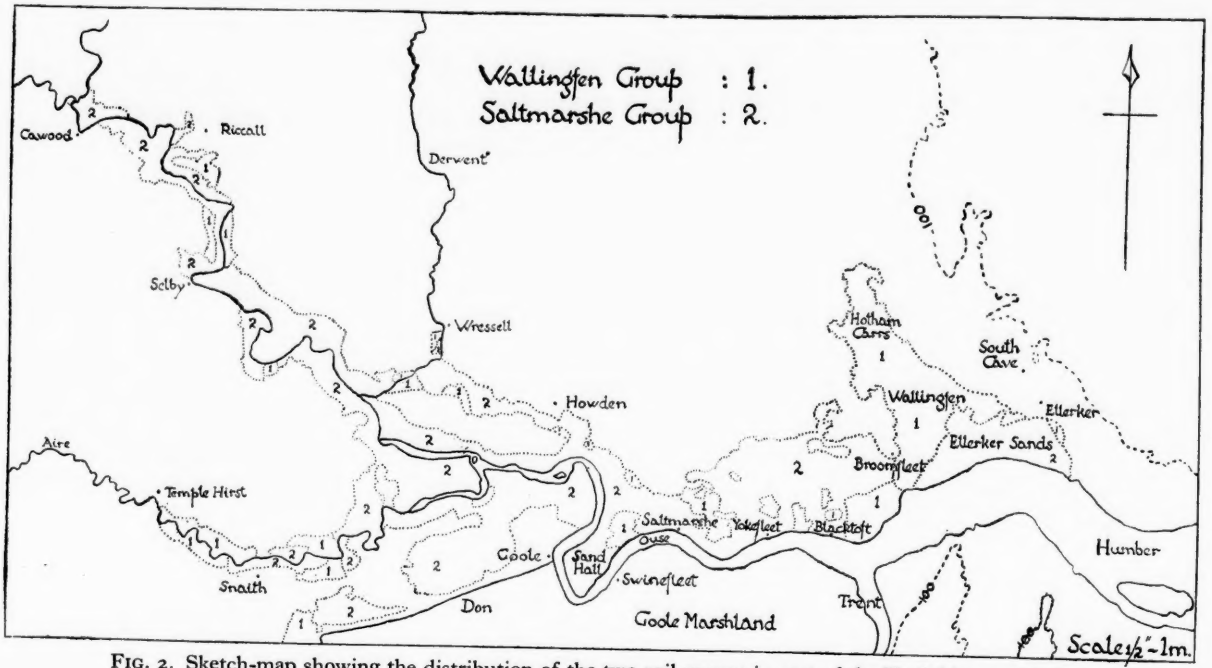

FIG. 2. Sketch-map showing the distribution of the two soil groups in part of the Yorkshire warpland.

Series develops, and the sharp boundaries of this series and its occurrence in single fields or groups of fields is explained. These fields are frequently situated between the Saltmarshe Series and the higher ground, the surface run-off from which contributes to the poor superficial drainage conditions. This is commonly accentuated by several separate and later warpings of land nearer to the river, raising it considerably in relation to the older warped land farther from the river. Soils of the Wallingfen Series frequently surround particularly low-lying areas where the Gowthorpe Series appears.

By grouping the three series in the Brown Earth group and the two series in the Gley group it is possible to portray the soils of the area quite adequately on a simple small-scale map (Fig. 2) both from a practical farming and from a pedological point of view.

Discussion of the Chemical Analyses

Well-established methods were used for the estimation of exchange capacity and pH. For the determination of free sesquioxides the biological reduction method of Allison and Scarseth (1942) was chosen. As most of the warp soils are highly calcareous, certain modifications were introduced to obtain complete reduction of the free iron oxides. According to the authors a pH of 3·0 is desirable and this, and complete reduction, may normally be obtained by anaerobic incubation in a few days. However, due presumably to the neutralizing action of the calcium carbonate present, the pH did not go much lower than 5·0, but complete reduction as evidenced by the grey colour was obtained by longer incubation. In some cases a further short incubation period was needed after the iron-rich liquid had been removed and a further supply of nutrient solution ('Analar' sucrose in distilled water) had been added. The concentration of iron in the final solution was determined by developing a coloured complex with thioglycollic acid and measuring the intensity of the colour using a Spekker photo-electric absorptiometer.

It is well to emphasize here that the finer fraction of the soil results from the attrition of deposits already well weathered, as much of the basin of the Ouse is covered with well-mixed and fairly far-travelled glacial and post-glacial deposits derived very largely from sedimentary rocks. This pre-deposition weathering may account for the rapidity of profile development where conditions are suitable. It may also account for the small change which is found in the exchange capacity of some of the lighter soils in which there is no concentration of clay in any particular part of the profile, for the fine sand is almost pure mica which is presumably fairly resistant to further weathering.

A selection of the chemical data is given in Tables 1 and 2.

pH. In general this value is high in the well-drained soils (Table 1, Nos. 6, 13, 17) and rises with depth. In the case of No. 13, which shows two depositions with a considerable time interval between them, the pH shows no pronounced change at the morphological break (27 in. depth).

The pH of the mud (Table 2, No. 21) is somewhat higher than that of any of the soil surface horizons. In the gley soils (Table 2) the pH

TABLE 1

Series and date of deposition	*Profile No. and horizon*	*pH*	$CaCO_3$ %	*Clay* %	*Exch. cap. m.e. per 100 g.*	*Exch. Mg. m.e. per 100 g.*	'*Free*' Fe_2O_3 *mg. per 100 g.*
Saltmarshe 1650	No. 6: A 0–13 in.	8·33	8·3	36·3	15·6	1·96	17·4
	B_1 13–19 in.	8·46	8·2	31·2	10·2	1·54	18·5
	B_2 19–27 in.	8·51	9·7	31·5	12·0	2·52	19·0
	C > 27 in.	8·53	6·2	15·8	6·7	2·05	15·7
1750	No. 13: A 0–5 in.	7·61	1·1	28·1	25·4	4·98	23·0
	B_1 5–11 in.	8·38	3·1	27·9	17·3	4·83	18·0
	B_2 11–20 in.	8·42	2·8	43·6	22·9	6·67	27·2
	C 20–27 in.	8·66	9·3	26·6	10·4	3·31	21·0
	A_1 27–31 in.	8·62	10·5	36·7	10·9	4·93	27·7
	B_1 31–38 in.	8·65	7·1	38·5	16·1	5·56	25·0
	C_1 > 38 in.	8·74	10·7	18·7	6·2	3·32	16·0
Blacktoft 1830	No. 17: A_1 0–9 in.	8·17	3·7	51·2	28·9	5·65	30·5
	B_1 9–20 in.	8·46	8·9	50·5	19·2	5·58	27·2
	B_2 20–33 in.	8·58	10·3	48·4	15·1	7·09	28·5
	C > 33 in.	8·63	9·0	38·2	12·8	7·01	25·7

TABLE 2

Series and date of deposition	*Profile No. and horizon*	*pH*	$CaCO_3$ %	*Clay* %	*Exch. cap. m.e. per 100 g.*	*Exch. Mg. m.e. per 100 g.*	'*Free*' Fe_2O_3 *mg. per 100 g.*
Wallingfen 1850	No. 19: A_1 0–7 in.	6·08	2·1	39·3	25·0	5·04	37·5
	G_1 7–10 in.	7·10	1·4	51·8	21·2	6·24	60·5
	G_2 10–15 in.	8·14	1·8	32·4	12·5	6·45	28·2
	G_3 15–21 in.	8·46	5·0	27·4	8·5	4·61	70·5
	C_1 21–29 in.	8·51	4·7	30·2	10·9	4·72	37·6
	C_2 > 29 in.	8·48	3·8	29·3	9·4	4·55	32·1
Before 1250	No. 20: A_1 0–4 in.	5·47	nil	49·4	36·8	6·70	10·7
	G_1 4–9 in.	6·28	,,	58·5	27·6	7·90	29·9
	G_2 9–20 in.	7·19	,,	50·6	22·3	8·16	45·5
	G_3 20–26 in.	8·12	,,	43·9	19·0	9·22	60·1
	C > 26 in.	7·63	,,	53·4	23·4	9·64	36·7
Gowthorpe 1923	No. 2: A_1 0–10 in.	8·28	n.d.	41·1	18·0	3·53	21·5
	G_1 10–17 in.	7·67	,,	50·3	33·5	4·79	26·9
	G_2 17–27 in.	7·28	,,	60·1	35·7	5·29	32·4
	C 27–31 in.	6·90	,,	n.d.	42·0	8·34	10·2
1820	No. 18: A_1 0–7 in.	5·68	nil	n.d.	43·3	3·48	28·2
	G_1 7–14 in.	6·62	,,	,,	28·5	3·57	38·0
	G_2 14–24 in.	6·66	,,	,,	28·1	4·25	42·2
Mud contemp.	No. 21: 0–6 in.	8·36	n.d.	n.d.	13·0	7·41	15·7
Saltings recent	No. 16: 10–12 in.	8·24	n.d.	n.d.	17·8	6·29	19·0
	22–24 in.	8·44	,,	,,	13·9	6·04	24·2
	34–36 in.	8·72	,,	,,	13·7	6·41	18·2

again rises with depth with one exception—profile No. 2, Gowthorpe Series, where the higher surface value is due to added lime. This group of soils shows a much greater leaching than do the well-drained soils, and it is only in the deeper layers that carbonate is present in appreciable amounts if at all. Profiles Nos. 18 and 20 have been undisturbed under grass for a long time and are characterized by acid surface layers.

Exchange capacity and adsorbed cations. An X-ray examination of the clay fraction ($< 2\mu$) from the mud (No. 21) and from the G_1 horizon of No. 19 (Wallingfen Series), by Mr. G. Brown, showed a trioctahedral hydrated illite (55–60 per cent.), kaolinite (*c.* 35 per cent.), with a small amount of a chloritic material. No account is here taken of possible amorphous matter. A comparison of the exchange capacities and clay content in Tables 1 and 2 gives values of 30–50 m.e./100 g. clay, which although high are not altogether unreasonable for the above mixture allowing for the presence of some organic matter.

The establishment of a plant cover on the mud leads to a marked increase in the exchange capacity by the addition of organic residues and the promotion of an increased rate of weathering. This is readily seen from the data for the mud and the upper sampled layer of the saltings. Another factor affecting the exchange capacity of the whole soil is, of course, the clay content, which can be seen from the tables although the relationship is probably in part masked by organic matter. The 'double' nature of profile No. 13 (Table 1) is clearly brought out in the exchange capacity figures, the B horizon showing higher values for each of the two components.

In the profiles of the gley soil group (Table 2) the exchange capacity is in general higher in proportion to the amount of clay than in those of the Brown Earths. This is probably in part due to somewhat higher organic matter content, although the X-ray data suggest a slightly higher proportion of illite to kaolinite. In the case of profiles Nos. 18 and 20 which have been under long-established turf the exchange capacity of the surface soil is high and highest where there is greatest accumulation of organic matter (No. 18). In comparing the two profiles of the Gowthorpe Series (Nos. 2 and 18) the effect of a long period of intensive cultivation on profile No. 2 in reducing the amount of organic matter and hence the exchange capacity is clearly shown. The heavy liming noted above has perhaps stimulated the loss. A similar effect of cultivation can be seen in the two Wallingfen soils, No. 20 having been long uncultivated while No. 19 is under ordinary rotation cropping.

It has been pointed out several times that the process of gleying leads to a marked increase in the amount of exchangeable magnesium in a soil, and this is indicated by the results given in Tables 1 and 2. The very well-drained profile No. 6 shows quite a low exchangeable magnesium (12 per cent. of exchange capacity) in the surface layer, rising slowly to a maximum in the C horizon (30 per cent.). Profile 13, on the other hand, which shows somewhat more mottling throughout, has 20 per cent. in the surface rising quickly to 30 per cent. at the 11-in. depth. Increasing mottling (No. 17) in the deepest layers is reflected in a very high proportion of exchangeable Mg (up to 50 per cent.) which is quite a feature of the very strongly gleyed profiles of the Wallingfen group (Table 2).

The age of the soil would seem to be a factor in this connexion, for it will be noted that the saltings (No. 16) shows a very high proportion of Mg, but this young soil is quite well drained. There is also a small amount of water-soluble magnesium (*c.* 1 m.e.) in both the saltings and in the mud.

Water-soluble sodium chloride is present in the more recent soils, as is shown by the following figures. The gradual loss of this constituent with time is also indicated.

TABLE 3

Soil Series	*Date of deposition*	*Depth*	*Water-sol.* Na *m.e./100 g.*
Saltings No. 16	Recent	10–12 in.	4·37
		22–24 in.	3·96
		34–36 in.	2·76
Saltmarshe No. 12	1900	10–12 in.	0·62
		22–24 in.	0·78
		34–36 in.	2·20
Saltmarshe No. 11	1850	10–12 in.	0·11
		22–26 in.	0·32
		34–36 in.	0·84

Free iron oxides. The free iron-oxide content of the mud is comparable with that of the C horizons of the profiles of the Saltmarshe group. In all the other horizons there has been an increase with weathering and profile development. This is shown most clearly in the Saltings profile (No. 16) where there is more free iron oxide than in the mud and even an apparent movement from the A to the B horizon (Table 2) which is noticeable in several of the profiles.

As with exchange capacity, the variations in free iron-oxide content follow clay content, since the free sesquioxides generally occur in the finest fraction. The humus provided by the grasses growing on the Saltings will help to increase biological activity and thus help the movement of iron in the soil, as the movement of and the changes in iron compounds in the soil are much affected by the amount and nature of the biological activity present (Ignatieff, 1940; Bloomfield, 1950). Free iron-oxide figures for the surface horizons of the other profiles also show the influence of organic matter and biological activity. Thus in profile No. 6 the turf cover is thin and composed of the fine grasses found in dry situations, while in profile No. 13 the turf is thicker, the grass cover more abundant, and the profile not as dry. In profile No. 17 organic matter is most abundant under a luxuriant growth of coarser grasses, although the soil also has a higher clay content.

It is apparent that a very much greater amount of 'free' iron oxide is typical of gley soils as compared with Brown Earths. This is in part due to the higher clay content of the former. The effect of organic matter and biological activity is seen very clearly in the surface horizons of the two Wallingfen profiles. Horizon A of profile No. 19 shows a high figure connected with a newly reseeded turf, and the very low figure for profile No. 20 with an old dead matted turf, the root development of which has been severely restricted by the close proximity of the gley horizon.

In the Gowthorpe profiles there is a high content of 'free' iron oxides that increases steadily with depth. In both Wallingfen profiles and in the Gowthorpe profile No. 2 there is a marked increase to the lowest G horizon and a very sharp drop to the C horizon. In the G horizons of profile No. 19 there is a marked periodicity in the content of 'free' iron oxide. This is also evident, though in a much lesser degree, in the Brown Earth profile, No. 13, but how far this is due to incipient gley development or to the double profile cannot be decided. The effect may, however, be compared with that noted by Glentworth (1949) for the SiO_2/Fe_2O_3 ratios in certain poorly drained Scottish soils. The very high figures for 'free' iron oxide, however, are only found where gley colours, blue, grey, and rust, are dispersed and not where there are concretions or heavy iron staining. This is especially striking between horizons G_1, G_2, and G_3 in profile No. 19.

There is an apparent slight leaching of free iron sesquioxide to the B horizons of the Brown Earth soils. Although slight, it is present in both light and heavy soils and to as great a degree in the very immature Saltings profile as in one of the Saltmarshe profiles which has been developing for 200 years. Age seems to have as little effect in the gley soils of the Wallingfen Series, but in the older Gowthorpe profile, the amounts of 'free' iron oxide are greater than in the younger profile.

While certain of the gley horizons show a very high value for 'free Fe_2O_3', it is improbable that very much of the iron is actually in a fully oxidized state in these layers. In fact, most of the blue-grey horizons revert fairly rapidly to a brown colour and only occasionally is the grey colour stable. This stability is most probably associated with the amount of readily soluble ferrous iron. The clay from the A horizon of the Wallingfen soil (No. 20) which shows the lowest 'free Fe_2O_3' has a very stable slate-grey colour even after peroxidation, while that of the G horizon reverts to brown on simple exposure to air.

Soil-fertility data. From an analysis of the figures of soil-fertility samples obtained from nearly 200 fields and analysed for lime, available phosphate, and potash, there is a clear difference between soils of the Saltmarshe and Wallingfen groups. The greatest difference is in the lime requirement, the percentage of fields in the Saltmarshe group with a requirement of half a ton or more being only one-third of that in the Wallingfen group. Moreover, only once in the Saltmarshe group does the lime requirement reach 30 cwt./acre; it is generally little more than 10 cwt.

In the Saltmarshe group the percentage of fields with a high phosphate content is nearly one and one-third times greater than in the Wallingfen group, and the number with a medium content is also much greater. Low phosphate values are only half as numerous in the Saltmarshe as in the Wallingfen group.

There is not so much difference in the values for potash in the two groups, but over the whole range of figures the fields of the Saltmarshe group have the more satisfactory potash content.

It is clear, therefore, that dividing the soil series into two groups is further justified by the relative fertility of each group as shown by these

analytical data. The small-scale, two-group map should thus be of value to those advisory officers working in the warpland.

Relationship between Soil Series and Warping Practice

Locally only the light soils of the Saltmarshe Series are recognized as 'good' warp and the heavier soils of the Blacktoft Series are regarded as 'poor' warp. There is no doubt that some of the reputedly best warpland overlies peat in Goole Marshland, but much of this has been warped several times. After the first warping early in the nineteenth century the land slowly sank, and the farmers, recognizing the necessity of maintaining the surface at a sufficient height above the water-table, had the land warped again and if necessary a third time. In Hotham Carrs there was only one warping and when, with gradual compaction, the land became lower and wetter, a soil of the Gowthorpe Series developed, and it was abandoned for arable cultivation and left for natural causes to make it into a meadow. Where, despite the weight of warp, the permanent water-table has remained in the peat and only occasionally rises into the warp, the result is satisfactory, the soil being of the Saltmarshe Series.

On the other hand, where the water-table stands so near the surface of the peat that it can rise into the warped soil soon after compaction, the result is unsatisfactory and the soil is classed as of the Gowthorpe Series. Thus at Hook Lane (profile No. 2) a group of fields in which the water stood at the surface of peat was warped in an attempt to improve them, but only about 24 in. of warp was deposited before the land was cultivated. The permanent water-table is therefore never very far below the warp soil, and seasonally rises into it with the result that the Gowthorpe Series has quickly developed.

In Goole Marshlands the Saltmarshe Series predominates, with light, very fine sandy clay loam soils. There is no conclusive evidence to show whether the lightness of the texture is due to the finer particles having been washed through the profile into the underlying peat or sand, or whether the warping water was never still long enough for the silt and clay particles to settle. There is some support for the former hypothesis (Thornton and Herapath, 1850), as in one place at least an enriching of the underlying sandy layers in clay has occurred.

On the north bank of the River Ouse where much of the warp is on lacustrine clay a heavier soil has developed, as in the Blacktoft Series. This may be due to the presence of the underlying slow-draining clay, but account must be taken of the fact that the original land surface stands high, so that much of the coarser fraction would be lost in the warping drain before the water reached the field and would be washed away with the returning outflow. Wherever the water was moving faster, as in the runs on to the fields, there is the lighter warp of the Saltmarshe Series. Much of the later warping is unsatisfactory because only 12 to 18 in. were laid down. Two factors are responsible for such thin warp being unsatisfactory; the deep cultivation favoured mixes undesirable underlying material with the warp soil, and in such thin warp with a high water-table gleying is rapid.

The Wallingfen Surface Water Gley soil occurs on warp of all textures and on all the underlying formations, and its development can only be ascribed to lack of adequate drainage.

A Note on Agricultural Practice

The deleterious effect of inadequate drainage on soil fertility has been amply proved and is reflected in the type of farming practised. Before 1939 the Wallingfen Series was farmed in much the same way as the gley soils on the nearby lacustrine clay. There was a general air of neglect, with many poor grass fields, a few weedy fields kept for arable cultivation, tall ill-kept hedges, overgrown ditches, and choked drains. Today the land is better farmed, but there is still a large acreage of permanent grass. This is in direct contrast to the farming on soils of the Saltmarshe and Blacktoft Series, where there is never more than one small home paddock under grass and seldom any temporary grass. Even during the worst of the depression these soils were well farmed under arable crops. The emphasis is on cash crops—potatoes, sugar-beet, peas for packeting, mustard for human consumption, wheat and oats, with a small acreage of 1-year seeds. The by-products were at one time used for fattening large numbers of bullocks in yards in winter, but this is not now so commonly practised.

As the soil is naturally very fertile, new warp was at one time farmed for some years without fertilizers of any kind, and certainly for the first few years crops are so heavy that they are difficult to handle. Now, however, the warplands are farmed with due attention to keeping the land in good 'heart' as continued cash cropping has created many difficulties, not the least of which is the potato eelworm which badly infects many of the lighter soils of the Saltmarshe Series, particularly south of the river.

Summary

1. Warp is a local term referring to the sediment carried in the Humber and the lower reaches of its tributaries, or to that sediment after it has been deposited on land flooded by the river.

2. A soil survey has been made of part of the Warpland, and the speed and intensity of profile development including that under conditions of impeded drainage have been investigated.

3. (*a*) There are three essentials without which artificial warping is impossible: (i) A tidal régime giving a high and rapid rise in river level with a longer ebb. (ii) Land suitable for warping within a reasonable distance of the river and lying between the levels of high and low tide so that a continuous sequence of rapid flooding and draining is possible. (iii) A heavy load of sediment in the river and lying unconsolidated on the bed and banks. (*b*) To ensure success artificial warping must be carefully planned and controlled. (*c*) An average of one-tenth of an inch of warp is deposited per flooding and in a good year a thickness of from 2 to 3 ft. may be obtained.

4. (*a*) The parent material of the soils mapped is *warp*, a highly calcareous micaceous deposit ranging from a fine sand to a silt clay or

clay. (*b*) The texture depends upon the speed of flow of the water when the deposit is being laid down.

5. (*a*) Warp may be deposited unconformably on sand, peat, or clay. (*b*) The underlying formations play only a minor role in profile development.

6. The soil series occurring have been classified as belonging to the following groups:

Brown Earth with gleyed B and C horizons { Saltmarshe Series. Blacktoft Series. Staddlethorpe Series.

Surface Water Gley—calcareous: Wallingfen Series.

Ground Water Gley—non-calcareous: Gowthorpe Series.

7. Each series is a 'mature' soil and not a transition phase to one of the other series named or to some entirely new soil or group.

8. The two groups, Brown Earths (Saltmarshe group) and Gley Soils (Wallingfen group), are shown on a small-scale map and clearly show the relationship between soil series and farming practice.

9. From evidence in the field it is apparent that drainage is the chief factor in determining profile development, while the varying texture of the parent material is of secondary importance.

10. (*a*) For warping to be efficient the land surface must be raised by warping sufficiently high above the water-table to obviate ground-water gleying. (*b*) Subsequent drainage both by ditch and tile must be efficient to prevent the accumulation of surface water and the subsequent development of surface-water gleying.

11. The freely drained soils support intensive arable farming with emphasis on cash crops. Where gleying occurs there is a marked deterioration in soil fertility, and in the standard of farming.

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NOTES ON THE SOILS OF SYRIA

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With five plates

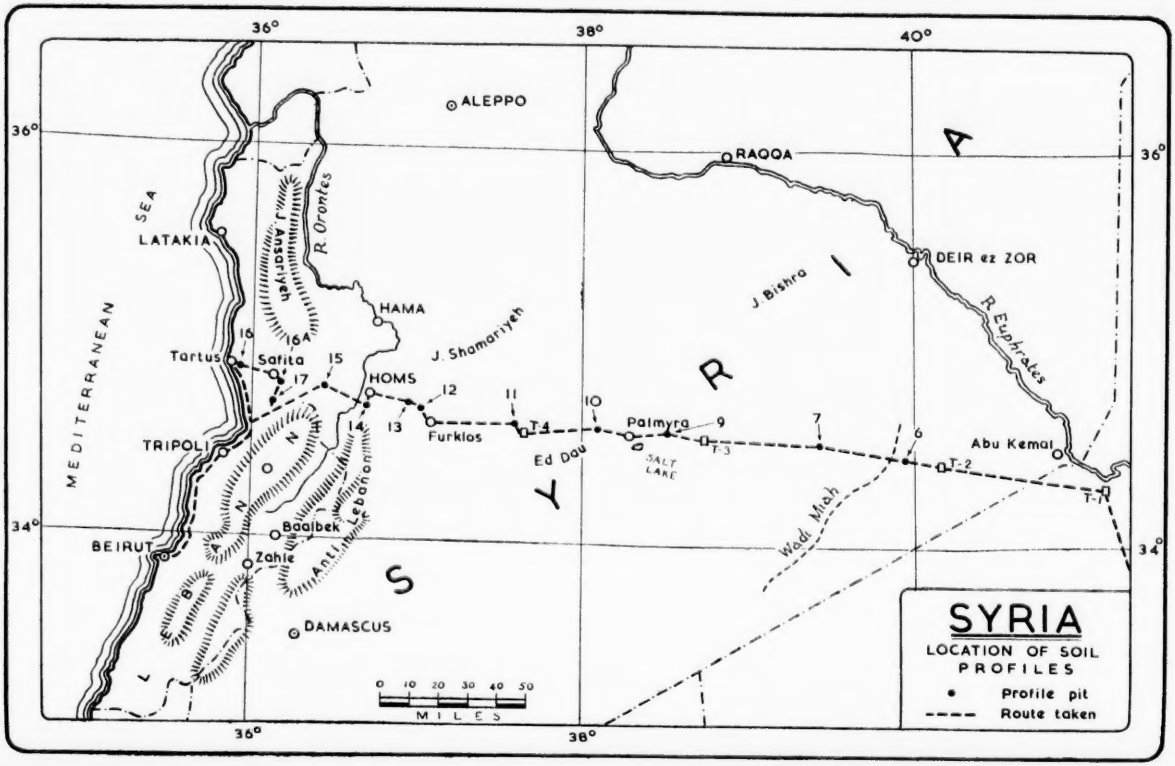
THERE has apparently been no modern study of the soils of Syria, although those of the Western Desert have been briefly described by Zohary (1940). One finds innumerable references by travellers to the nature of the surface and occasionally to the colour of the soil, e.g. Musil (1928), and the descriptions of desert crust by Blankenhorn (1914) have been much quoted (Glinka, 1931; Joffe, 1949); Blankenhorn was, however, a geologist and not really concerned with the soil. In a recent book on peasant life in Syria (Weulersse, 1946) the author can write that 'pedology in general is a young science; Syrian pedology in particular has still to be created'. Nevertheless, this writer gives a reasonable sketch of the soils based on geology only. In Palestine, on the other hand, a considerable amount of work has been done by Reifenberg and other workers (Reifenberg, 1947; Rim, 1950; Zohary, 1942), much of which is quite applicable to Syrian conditions.

The following account of Syrian soils is based on a journey by Sir W. G. Ogg and the writer of some 400 miles across the desert from Iraq to the Lebanon. From Baghdad to the Syrian frontier near Abu-Kemal our route followed approximately that of the 'Great Desert Route' (Grant, 1937) and then turned west into the Little Desert or Palmyrena (Musil, 1928), through Palmyra to Homs and thence to the Mediterranean coast. Our journey was made possible by the Anglo-Iranian Oil Company with the co-operation of the Iraq Petroleum Company, to both of which we are much indebted for all the facilities they made available to us.

General Physical Features and Geology

Syria may be regarded as a great tableland sloping gently to the east and north-east. Along its western edge the rocks have been rucked up to form the Lebanon and Anti-Lebanon Mountains which rise to 10,000 ft. at the highest point. Another area of high ground is formed by the basalt flows of the Jebel Druze.

In the Lebanon the mountains come steeply down to the sea, but to the north of Tripoli there is a well-developed coastal plain backed by the Jebel Ansariyeh range. Between the Lebanon and Anti-Lebanon Mountains lies a narrow trough carrying the Orontes River to the north and the Litany to the south, both rivers breaking sharply through the mountains to reach the sea. The Anti-Lebanon range, running parallel to the Lebanon in its southern and highest parts, bends away to the east near Homs, forming a rolling downland, and fades out in the Jebel Bishra near Deir ez Zor on the Euphrates. From the neighbourhood of Damascus a series of ranges known as the Kalaman Ridges extend north-eastwards to Palmyra.


36°
38°
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ALEPPO
RAQQA
LATAKIA
SEA
MEDITERRANEAN
R. Orontes
Jebel Ansariyeh
HAMA
DEIR ez ZOR
J. Bishri
R. Euphrates
Tartus
Safita
HOMS
J. Shamariyeh
TRIPOLI
Furklos
Palmyra
Ed Dau
SALT LAKE
Abu Kemal
Wadi Mah
BEIRUT
Baalbek
Zahle
Anti Lebanon
DAMASCUS
SYRIA
LOCATION OF SOIL PROFILES
Profile pit
Route taken
0 10 20 30 40 50
MILES

To the north-east and north of these various ranges the gentle slope of the desert is broken by a pronounced escarpment to the south and east of Palmyra, and along the northern edge of the J. Bishra.

While large stretches of the desert are fairly flat it is deeply and extensively cut by large wadis. Some of these, however, appear to be no longer actively excavating their beds and their upper slopes are rounding off to give a down-like topography. Numerous small depressions occur in the plateau, and two well-defined basins occur near Palmyra which lies in one of them.

The Syrian tableland can be regarded in the main as a great limestone plateau with the oldest rocks in the west and the youngest in the east. The Lebanon and its associated ranges consist of Cretaceous rocks which have been locally eroded to expose the underlying Jurassic. Massive crystalline limestone is the predominant parent rock for the soils of these mountain areas. The greater part of the desert plateau consists of Eocene and Miocene limestones, with Cretaceous materials exposed in the Kalaman Ridges and the J. Bishra. Gypseous and marly facies are common. Deposits of Pliocene and more recent age (e.g. recent alluvium) occur in the Palmyra and Ed Dau depressions and in the Orontes Valley and also in the Coastal Plain. Basaltic lavas of fairly recent age are prominent between Homs and the sea, and cover a still greater area in the J. Druze in the south-west. These vary considerably in the degree of crystallinity, to which further reference will be made later.

Climate and Vegetation

In winter the Mediterranean forms a channel through which flow depressions from the North Atlantic, bringing the rain caught by the Lebanon Mountains. In summer the high-pressure system of the Azores extends its influence to the east, while the cyclonic areas in the Indian Ocean reach only the southern tip of Arabia. During this period the central part of the peninsula suffers drought and torrid heat. This is modified a little on the coast and temperatures rarely reach those of the inland region.

Along the coast the rainfall averages about 30 in., falling mainly in the winter—November to February, with moderate amounts in March and April. July and August are generally rainless. The rain-shadow cast by the Lebanon ranges is very sharp and at Homs and Aleppo the rainfall has dropped to about 15 in., again coming entirely in the winter. Farther inland to the south and east beyond the Anti-Lebanon the annual precipitation again decreases sharply to values of less than 7 in. At Palmyra the annual fall is about 5 in., all coming between October and April. This figure seems to be representative of the greater part of the north Syrian desert.

While the annual and diurnal variation in temperature on the coast is lowered by presence of the sea, there is no such beneficent influence in the desert regions and here the mean monthly temperatures range from about 5° C. in winter to 35° C. in summer. Frosts are extremely rare on the coast, but are not uncommon in the desert. Absolute summer maxima in the higher desert may reach 44° C.; in the Euphrates Valley

even this is exceeded by several degrees. On the coast absolute maxima may reach 40° C.

In the vegetation of Syria three well-marked zones can be recognized: the Mediterranean zone, the steppe, and the desert. There is sometimes inserted a fourth—the desert-steppe, but it is rather ill defined. The Mediterranean zone can be subdivided into the littoral and the mountain areas.

On account of the coincidence of the hot and dry seasons the vegetation of the littoral zone is characterized by plants that can withstand considerable drought. Among the shrubs and trees both evergreen and deciduous oaks are common, but practically all the high forest has been cut, and the present-day woodland consists mainly of the secondary *maquis*. In the mountain zone both Aleppo and stone pines and the well-known cedar flourish. The littoral zone is largely under cultivation, and even in the mountains terraced agriculture is practised up to 5,000 ft.

The boundary between the Mediterranean and the steppe and desert zones can be taken as approximately that of the 20-in. isohyet, this being about the limit of spontaneous growth of forest. Zohary (1940) describes this steppe and desert as Irano-Turanian territory which is characterized by several well-defined communities. The principal one is that of *Artimesietum herbae-albae*, which covers a great part of the more desertic part of the area and extends up the Anti-Lebanon to 5,000–6,000 ft. This community occurs in two aspects: that of spring being characterized by numerous annuals including *Poa sinaica*, whereas that of summer consists of *Artimesia* alone. The mountainous areas of the J. Druze, the Anti-Lebanon, and the Kalamon ridges carry *Pistacietum atlanticae* sometimes in the form of park forest together with *Artimesia* and *Haloxylon*. In the vicinity of Homs, Hama, and Selemiyeh there is a transition type between the Mediterranean and steppe characterized by *Asphodelus microcarpa* and other non-steppe plants. While the change from steppe to desert is not sharp vegetationally it is fairly well marked by the limit of regular cultivation.

The Soils

Broadly one can recognize about ten major soil groups in the region. Of these, three occur in the desert area, viz.

(*a*) Brown desert soils.
(*b*) Solonchakous brown desert soils.
(*c*) Undeveloped soils on alluvium.

It seems possible to separate a group characteristic of the more steppe-like zone.

(*d*) Grey and brown steppe soils.

From the coastal plain to the Anti-Lebanon range three main groups may be distinguished:

(*e*) *Terra rossa*.
(*f*) Brown soils on basalt.
(*g*) Gley soils on alluvial flats, including swamps.

Along the coast there occurs a reddish sandy soil which seems to consist of blown sand over *terra rossa* (cf. Reifenberg, 1948), and in the Lebanon brown forest and podzolized soils occur at the higher elevations.

Variations occur within some of these groups depending on the parent material. Local erosion affects the depth of soil and also the texture of the surface, but on the whole the morphology in each group seems to be fairly constant.

(a) Brown desert (steppe) soils (Reddish desert soils)

These are characterized by the so-called desert mulch on the surface, which is also frequently strewn with stones bearing a black or reddish desert glaze (varnish). Under the mulch the soil tends to form an unstable crust of an inch or so in thickness. The soils are all highly calcareous, but no definite instance of desert crust or *croûte calcaire* was seen. It is possible, however, that what was taken to be weathered limestone at the base of some of the soils may in fact have been the crust. Blankenhorn (1914) reported the crust to the north of Homs, and Mr. W. Whalley of the I.P.C. has, since our visit, informed us that he has encountered this feature in an area of unconsolidated deposits to the east of Palmyra. Plate I, Fig. 1 shows a typical view of the Brown Desert soil region.

In general the soils we examined appeared to be derived directly from limestone or gypseous rocks. They are mostly shallow, the rock being reached at about 36 in. or less. The following profile description is typical of a large area in the desert.

I.S. 6

Site: Flat area with very slight depressions, 8 miles W. of T2. Elevation: 1,400 ft. Vegetation: Scattered *Artemesia*, some *Helianthemum*, and a little grass.

A_1	0–2 in.	Thin ($\frac{1}{8}$ in.) crust, which cracks on drying and bears a few white lichen (?) spots, over dull light brown (7·5 YR7/4 dry; 5 YR 5/8 moist) calcareous loam, greyish cast on drying; ill-defined platy structure; main root zone, but roots not abundant.
B_2	2–9 in.	Dull light brown (7·5 YR 7/4 dry; 5 YR 5/6–4/6 moist) calcareous loam; porous, rather hard nutty structure; insect (?) holes; a few nests of carbonate, few roots, few stones.
B_3	9–32 in.	Light brown (7·5 YR 7/6 dry; 5 YR 4/6 moist) calcareous loam; fairly compact, but porous; indefinite nutty structure; some nests of carbonate; few roots or stones. There is much gypsum at the bottom of this horizon.
C(?)	32 in.+	Limestone.

The Munsell colour designations are based on laboratory examination as the charts were not available in the field. The reddish tinge in most of the soils is noticeable and in one pit the subsoil had almost a *terra rossa* colour (2·5 YR 5/3–4/6). The sandy mulch varies in colour from pinkish to yellowish.

The highly calcareous nature of the Palmyrean soils and their lack of well-marked horizon development is presumably due to long-continued arid conditions and to erosion continually renewing the top soil.

The soils are invariably highly calcareous right to the surface and to a varying extent gypseous, especially near the bottom of the profile. The

carbonate appears to be disseminated through the various mechanical fractions, and in the field the soils seem lighter in texture than the mechanical analyses suggest. Some analyses show a slight increase in clay content with depth, but there is little evidence of translocation of clay, although there is sometimes a slight compaction in the subsoil.

The ill-defined platy structure in the top 2 in. is quite characteristic of the soils in the region, and may be still discerned when the surface has become buried under drifting sand. The nutty structure of the second horizon in the above profile is not a constant feature of the soils; it is sometimes only feebly developed and is often absent. Small burrows occasionally occur in the subsoil.

The sand drift just mentioned appeared to be rather common, but only formed thin layers of not more than 2–3 in. on the older soil surface. The sand is usually trapped by the sparse shrubs and sometimes forms miniature barkhans around them up to 6–8 in. high. It is locally wind-rippled over quite large areas.

Some of the slight depressions are apparently slightly moister and carry a somewhat more luxuriant vegetation which, however, is not dissimilar to the general type. On such sites the soil structure is somewhat better developed, but the soils are otherwise similar to that described above.

In the vicinity of wadis generally, and locally elsewhere on elevated surfaces, erosion has been marked and the soils are very shallow (6–8 in. deep), either with very pebbly surfaces or rock exposed. In the wadi bottoms there are frequently terraces of variable mechanical composition. The finer alluvium has often a reddish brown colour and is of a silty loam texture. The soils seen on this material showed little or no profile development.

TABLE 1

Mechanical Analysis of Brown Desert Soil (I.S. 6)

(Per cent. of oven-dry soil)

Depth	*Coarse sand*	*Fine sand*	*Silt*	*Clay*	$CaCO_3$
0–2 in.	5·94	16·08	14·25	22·38	40·03
2–6 in.	4·77	14·67	15·50	26·13	37·00
15–18 in.	4·85	11·40	18·75	25·00	38·50
28–32 in.	7·26	12·62	11·50	19·51	50·80

In Table 1 are given the results of a mechanical analysis of the profile described above. The very high carbonate figure is perhaps the most striking value; the slightly higher result for the surface soil is typical of all those examined. Results for other profiles show a variation in the silt and clay relation, but the trends are as in the table. The soluble-salt content of this type of soil is usually very low and consists almost entirely of gypsum as is seen from the data given in Table 2. Occasionally gypseous bands occur, the gypsum content amounting to 30–40 per cent. of the soil.

TABLE 2

Water-soluble Salts in Brown Desert Soil (I.S. 6)

(Soil: water ratio 1:25; results as per cent. oven-dry soil)

Depth	*Total salts*	Ca	Na	HCO_3	CO_3	Cl	SO_4
0–2 in.	0·15	0·01	<0·03	0·16	nil	0·02	0·02
2–6 in.	0·30	0·04	,,	0·16	,,	nil	0·03
6–9 in.	0·15	0·02	,,	0·13	,,	,,	0·02
15–18 in.	0·30	0·03	<0·02	0·07	,,	,,	0·03
28–32 in.	0·20	0·04	,,	0·12	,,	0·01	0·05

An X-ray examination of the clay ($< 2\mu$) from several of these desert soils (I.S. 6, 7, 10) showed that the principal mineral was attapulgite with some kaolinoid and micaceous material. The differential thermogram also indicates attapulgite. In Plate IV are given a few electron micrographs* of the clay which show that the main constituent forms lath-shaped particles up to about $1–2\mu$ in length and about 0·05 to $0·25\mu$ in breadth. As seen in Fig. 2 (I.S. 7) the broader ones appear to be parallel aggregates of the narrower. The ends are usually fairly clean-cut, but a few are rounded or tapering. This material is exactly the same in appearance as a specimen of almost pure attapulgite obtained from Shetland by Mr. I. Stephen, apart from particle size.

The only report of attapulgite (paligorskite) in soils that we have seen is that by Michaud, Cerighelli, and Drouineau (1945) for a clay from *terra rossa* in the south of France. It does not occur in our samples of this soil type (see below) and has apparently not been observed by Kubiena (1948), or by Bramao, Cady, and Hendricks (1950) in their red limestone soils. It may be noted, however, that Millot (1942) in his study of French sedimentary rocks records attapulgite only from the Upper Eocene, while the attapulgite rocks in the U.S.A. are apparently of Miocene age. Both these formations occur extensively in central Syria.

Saline Soils

The topography of great stretches of the northern desert is such that only small patches of saline soils occur, but in the vicinity of Palmyra there are two great basins occupied to a considerable extent by these soils. The first of these lies a few miles to the east of that town and stretches in a SW.–NE. direction. The lowest point to the south-east of the town is occupied by a salt lake, but the ground rises fairly rapidly to the north-east so that towards T3 the soil though saline is not highly so. The second large area occupies a great part of the Ed Dau basin to the west of Palmyra.

Two main varieties of these saline soils can be recognized: in the first there is a somewhat hard crust which has a low salt content and carries a rather poor halophytic vegetation; in the second the crust is not hard and is quite salty with no vegetation. Apart from this surface difference,

* Film of clay deposited on glass, shadowed and coated with collodion. The whole is then stripped from the glass. This specimen is sometimes referred to as a pre-shadowed replica.

which appears to be due to small differences in micro relief, the soils are identical. The following profile is typical of the first variety:

I.S. 9

West of T_3, 10 miles. Elevation: 1,300 ft. Vegetation: occasional shrubs and abundant small halophytes. Locally some of the shrubs are partly sanded up.

0–2 in. Thin, hard, platy crust passing into slightly laminar silt loam; this layer is very porous; moderate number of roots, no stones.

2–6 in. Light brown silt loam tending to small cloddy structure; compact, porous, with many fine roots; scattered small white spots (carbonate); no stones; fairly sharp change to

6 in.+ Light brown silt loam, soft; sparse white spots; no stones. This layer extends to at least 48 in.

The whole soil is highly calcareous.

TABLE 3

Mechanical Analysis of Saline Soil (I.S. 9)

(Per cent. oven-dry soil)

Depth	*Coarse sand*	*Fine sand*	*Silt*	*Clay*	$CaCO_3$
0–2 in.	2·15	4·32	12·25	34·94	39·0
2–6 in.	5·24	5·35	5·05	42·16	34·0
15–18 in.	13·57	8·03	11·75	37·85	35·0
33–36 in.	6·60	7·04	8·50	33·40	37·0

The mechanical composition of the soil is given in Table 3, and it will be noted that the field estimate of texture is obviously governed by the calcium carbonate present. The marked increase in clay content in the sub-surface layer probably accounts for the increased compaction noticed, but we do not know how characteristic this is.

An X-ray examination of clay, separated from the soil without pre-treatment, shows abundant calcite, a small amount of a kaolinoid mineral, and a material which is probably attapulgite.

TABLE 4

Water-soluble Salts in Saline Desert Soil (I.S. 9)

(Soil: water ratio 1:25; results as per cent. oven-dry soil)

Depth	*Total salts*	Ca	Na	HCO_3	CO_3	Cl	SO_4
0–2 in.	0·60	0·07	0·09	0·13	nil	0·10	0·07
2–6 in.	0·85	0·05	0·19	0·07	,,	0·39	0·10
15–18 in.	1·30	0·07	0·31	0·14	,,	0·57	0·15
33–36 in.	1·65	0·06	0·39	0·10	,,	0·66	0·11

The data for soluble salts are given in Table 4, and these show the relatively low salt content in the surface soil with a rather sharp increase in the subsoil, especially in the chloride figure.

Grey and Red-brown Steppe Soils

The western boundary of the desert or desert-steppe makes rather a sinuous line starting at Meskne on the Euphrates and curving south-westwards and then south some 40 miles to the east of Homs, Hama,

and Damascus. Annual fluctuations in rainfall shift the desert edge of Fertile Crescent to and fro, but there is little permanent cultivation east of Furklos. Thus, at T4 during the years 1935–8 the rainfall varied from 4·4 to 7 in. Wherever suitable springs occur these are tapped as a source of irrigation water, as is done at Palmyra, Sukneh, and a few other places. A typical view of the rolling downland near the site of the profile described below is given by Plate I, Fig. 2.

In the more steppe-like region there is no striking change in the soils until the watershed of the J. Shomariyeh is reached to the west of Furklos. The underlying rock is in the main of rather soft limestone and there is still a stony pavement on uncultivated ground, the stones having a brown rather than black glaze. A noticeable change in soil structure, however, especially in the upper layers, begins to show up about T4 on the line of our route. The platiness observed in the desert soils disappears and a soft crumb structure takes its place. This is illustrated by the following profile.

I.S. 11

About 4 miles west of T4. Rolling relief, pit on gentle slope. Elevation: *c.* 1,500 ft. Vegetation consists of short grass, plantains, and other plants.

A_1	0–3 in.	Light brown (7·5 YR 6/6) loose loam, drying greyish, with dense mass of roots; stony (all flints); tends to form soft crumbs on drying; porous; merges into
B_2	3–6 in.	Similar in colour (7·5 YR 6/6), &c., but moister and tends to dry into soft clods; roots fewer; merges into
B_3	6–16 in.	Similar (7·5 YR 8/5), but fewer roots and fewer stones; passes fairly sharply into
B_4	16 in.+	Very pale brown (10 YR 8/3) loam, somewhat compact and locally cemented; very few stones. Seen to 36 in.

TABLE 5

Mechanical Analysis of Desert-Steppe Brown Soil (I.S. 11)

(Per cent. oven-dry soil)

Depth	*Coarse sand*	*Fine sand*	*Silt*	*Clay*	$CaCO_3$
0–3 in.	18·17	18·70	8·75	18·21	35·83
3–6 in.	16·88	16·83	8·10	20·11	37·00
13–16 in.	1·74	16·31	9·09	20·73	47·25
16–20 in.	1·31	3·30	2·78	12·90	25·00
28–32 in.	8·50	2·45	4·73	26·07	52·50

The whole soil is highly calcareous and the upper part of the last layer is highly gypseous, as can be seen from the mechanical-analysis results in Table 5 (16–20 in.). There is a marked variation in the stone content, probably as a result of deflation, and the surface is covered to about 70 per cent. with red-brown stained flints. There is no sign of clay movement.

Soluble salts were not determined on this soil since field resistivity measurements were high, suggesting that only very small amounts were present in the upper layers. Exchangeable sodium amounted to about 1 m.e. per 100 g. soil.

The underlying rock between T4 and Furklos is much more chalky, with bands of chert and flint, and shows up on the steeper slopes of the rolling down-like country. The soils take on a much greyer cast when dry, especially in the vicinity of Furklos, which lies on a broad undulating plain on the south-east side of J. Habli. The following profile is typical of this area.

I.S. 12

6 miles west of Furklos; site on lower end of low ridge. Cultivated (barley). Elevation: 2,000 ft.

A_p	0–3 in.	Plough layer; pale brown (10 YR 7/3 dry) sandy clay loam, stony; abundant roots; cakes slightly on surface; porous, numerous small holes and a few earthworms; merges into
B_2	3–15 in.	Similar, but more compact; roots sparse; merges into
B_3	15–24 in.	Pale brown (10 YR 6·5/3 dry) sandy clay loam, slightly darker than upper layers; stony, porous; few roots penetrate; merges into
C	24 in.+	Shattered soft limestone.

The whole soil is highly calcareous and there is a small amount of gypsum in the lower layers. There is no marked profile development even in the uncultivated soil.

No rainfall figures are available for the Furklos area, but it is presumably something of the order of 10 in., since it is just on the edge of the rain-shadow formed by J. Habli, an extension of the Anti-Lebanon. Cultivation of cereals is extensive. At the time of our visit the crops looked poor and very weedy. A. Musil, in recording his visit in 1912, remarks that the crops at Furklos were suffering from drought on the rather shallow grey soil. Where irrigation is possible crop growth is excellent both on the desert and the steppe soils.

On a broad climatic basis the soils described so far should correspond to those of the more arid south-eastern regions of the U.S.S.R., e.g. Turkistan, and to the drier parts of Arizona and California, e.g. the Mohave Desert area. There is, however, a marked difference in the distribution of rainfall. Except in the southern part of Turkistan, that region, like Arizona and California, has a moderately high summer rainfall, whereas in the Syrian steppe and desert there is no rain during the six months May to October. It might be expected that this would lead to important differences between the soils of these contrasting areas, but the high carbonate content of the Syrian soils has evidently in part, at least, impeded their development. The structural features that are shown suggest a strong resemblance between our first group of soils and the sierozems of Turkistan as described by Neustruev and Gerasimov (cf. Gerasimov, 1931). The soils described by the latter as structural sierozems usually have a rather stony surface and show a marked platy structure under a thin grey crust; the succeeding layer is brown and usually has a crumb structure, it becomes more compact with depth and gypsum separates. None of Gerasimov's soils occurred on limestone, but they were calcareous and showed a curious distribution of carbonate which was at a maximum in the surface layer. The vegetation consisted of *Artemesia*, *Anabasis*, and *Salsola* spp.—genera corresponding to those of the Syrian desert.

The platy structure in such arid soils is generally taken by Russian workers to imply a certain degree of solonization. There is a small amount of water-soluble sodium (*c.* 1 m.eq.) present in the surface layers of our profiles and the exchangeable sodium is about the same.

Since the platy structure in the Syrian desert soils is best developed on smooth or very slightly depressed areas, it would seem that the shifting of fine material by rain and wind is more likely to have caused the platy structure of the surface horizon.

In the desertic steppe region, e.g. around Furklos, long cultivation could be responsible for the lack of well-developed structure, and in addition wind erosion is likely to have been strong. But most of the soils described above are from areas that are far from any settlement and are unlikely ever to have been cultivated. There is a certain amount of blowing of fine material from and along the surface and the desert mulch is widespread. This mulch does, however, protect the underlying soil to some extent from further wind-blow. There are no areas of sand-dunes in the northern part of the Syrian desert, these apparently being confined to the southern area where granite and the Nubian sandstone outcrop.

It would seem, then, that the highly calcareous parent material together with erosion under what have doubtless been prolonged desert conditions have never permitted the development of anything beyond the rather juvenile profiles described. As regards the clay minerals of the soils, they are of types that could quite well have come from the underlying limestone and there is little or no change in the nature of the clay with depth.

It is generally considered that the steppe conditions extend to the west of Homs, Hama, and Aleppo (Zohary, 1940; Dubertret and Weulersse, 1940) since the 20-in. isohyet is taken as the limit of spontaneous forest. There are, however, one or two transition areas on the higher northern parts of the Anti-Lebanon chain in which the soils and vegetation have a distinct Mediterranean affinity. To the east of Homs and elsewhere on Cenomanian and Turonian (Upper and Middle Cretaceous) limestones there are developed red-brown soils, not unlike the *terra rossa*, which carry abundant asphodels and *Gundelia*. The soils are on the whole shallow, but show a marked variation in depth due to the manner in which the limestone has weathered out. The following profile seems typical of this group (Plate II, Fig. 1).

I.S. 13

10 miles west of Furklos on ridge of J. Habli. Elevation: 3,000 ft. Vegetation largely annuals with abundant asphodel.

A_1	0–6 in.	Red-brown (5 YR 6/4) calcareous clay loam, granular structure, abundant roots, stony; merges into
B	6–26 in.	Red to reddish-brown (5 YR 6/4–6) calcareous clay loam, somewhat granular structure; more compact than above; stony, few roots; sharply overlies
C	26 in.+	Fine-grained cream-coloured, hard, crystalline limestone with weathering crust.

Apart from the more rooty surface layer no clearly defined horizons

are shown by this soil. Carbonate is fairly equally distributed throughout the profile (41–46 per cent. $CaCO_3$) and there is little variation in the contents of the various mechanical fractions apart from a slight increase in sand in the upper layer. The granular structure is quite marked.

The exchangeable bases for this soil are shown in Table 6. The value for calcium is high because of the presence of carbonate and the somewhat high value for magnesium may be due to the same cause. The sodium content is low and the potash value only moderate.

TABLE 6

Exchangeable Cations in Red-brown Steppe Soil (I.S. 13)

(m.eq. per 100 g. oven-dry soil)

Depth	Ca	Mg	Na	K
0–3 in.	35·6	3·09	0·30	0·86
3–9 in.	39·3	3·12	0·31	0·59
9–12 in.	39·8	2·45	0·38	0·45
22–26 in.	37·8	2·34	0·37	0·35

The clay of this soil consists of chloritic and illitic minerals with some attapulgite, kaolinite, and quartz. The clay appears to be highly hydrated as judged by the high water peak obtained on the differential thermogram. No iron oxides are shown by the X-ray analysis.

An electron-micrograph (Plate IV, Fig. 3) of the oxalate-treated clay shows some rather rounded, almost spherical, particles and some thickish plates, with a large number of fragments of a fibrous mineral, which is the attapulgite component. The plates and aggregates are presumably the other constituents, in part still cemented together.

Along the line of our route to Homs the red colour in the soils appeared to become more marked, possibly due to the approaching Mediterranean climate, but perhaps also to slight changes in the parent rock. Such changes in the coastal region (i.e. hard or soft limestone) have a profound effect on the soils, giving either *terra rossa* or rendzina. This red-brown soil type resembles some seen in Algeria (Conference International, &c., 1947) overlying *croûte calcaire* which is much exposed by erosion. These Algerian soils were considered to correspond to the American reddish chestnut group and the same term could be applied to those of Syria, although there is no evidence of secondary carbonate in them. Until they have been more extensively studied it seems unwise to equate the red-brown steppe soils of Syria with the reddish chestnut soils of the U.S.A.

The red-brown steppe soils are extensively sown to cereals, and Plate II, Fig. 2 shows summer cultivation being carried out on them.

The town of Homs is situated at the inner end of a marked gap in the northern Lebanon range and on a broad alluvial belt forming the lower end of the Bekaa between the Lebanon and Anti-Lebanon through which flows the Orontes River. This alluvial plain stretches from about 20 miles south of Homs, northwards to Hama, where the river has to cut

a gorge through a basalt flow. Still farther north occur two other basins—the Ghab and the Amouk near Antioch.

The river is controlled at these various basins and at Lake Homs by a barrage that dates from ancient times. Extensive irrigation is practised for fruit and vegetables. Vines and nuts are also grown.

The alluvium is a drab brown, rather heavy clay loam, and is obviously of mixed origin. Near the river, however, it is almost black in colour due to the abundant oxide grains derived from the adjoining basalt. The water-table seems in general to be fairly high and the soils are slightly saline locally. There is no clear profile development, but an increase in grey and rusty mottling with depth is marked. The structure tends to be cloddy in the surface and roughly prismatic in the subsoil.

The mineral content of the clay fraction of the Homs soil shows no variation with depth. The principal minerals are kaolinite and a chloritic mica with some quartz and calcite.

A smaller area of this type of alluvial soil occurs in the Bouqaia about 20 miles west of Homs. The soil is a heavy clay, dark grey in colour, and appears to contain a considerable amount of basaltic material. Irrigation cultivation of rice, maize, and other crops is practised. The plain floods readily after heavy rain.

Terra Rossa *and Brown Soils on Basalt*

As pointed out in the section on the geology, the main rocks in the area under consideration are limestone and basalt, and the soils derived from these two materials stand out in the landscape in marked contrast to one another. Apart from a narrow strip of the coastal plain the *terra rossa* is confined in the main to the lower slopes of the more hilly country of the Lebanon and its northern extension, the Ansariyeh range. The basalt areas form smooth land-forms, although the surface of the ground, especially in the more inland portions, is covered with vast numbers of boulders. On account of the similarity of the basalt soils of the steppe near Homs to those of the coastal area they are here considered together. Both the *terra rossa* and the brown basalt soils are extensively cultivated.

The greater part of the Mediterranean zone is now denuded of most of the forest for which it was famous in early times, and apart from recent plantations we saw only some rather scrubby oak groves in the areas we visited. An interesting sidelight on the erosion of these red soils is provided by the account of the Festival of Adonis recorded in the *Golden Bough* (Frazer, 1922). After the heavy winter rains and the melting of the snow in the high mountains the River Adonis (Nahr Ibrahim), near Byblus, runs red to the sea and was taken by the Phoenicians to represent the (annual!) wounding to death of the god by a wild boar on Mount Lebanon.

The oak groves, even although they are probably secondary, were of considerable interest since under this vegetation a highly humose horizon was present above the red subsoil, the general morphology suggesting a brown forest soil on a red-coloured parent material. The following is a description of one example.

I.S. 16A

Near Safita. Elevation: *c.* 700 ft. Evergreen oak scrub.

A_0	1–0 in.	Oak litter.
A_1	0–6 in.	Black (2·5 YR 3/2), crumbly, humose loam; porous, abundant roots; earthworms; stony; merges through dull red-brown rapidly to
B–C	6–12 in.	Red clay (10 YR 3/6), granular structure, porous; roots frequent; mainly filling large interstices in rock.
D	12 in.+	Crystalline, fossiliferous limestone.

The fine material of the surface layer is non-calcareous but base-saturated, and there are innumerable small pieces of limestone scattered throughout. The red subsoil is only slightly calcareous apart from small stones. The clay content of this layer amounts to 67 per cent.

Zohary (1942, 1947) in his writings on Palestinian soils has described this type of *terra rossa* in areas densely covered with maquis and forests that are characterized by the climax association *Quercetum calliprini.* The ordinary *terra rossa* of the literature would correspond to what Zohary has described as that preserved or formed under open devastated woodland, under cultivation, or on eroded slopes. The destruction of the forest leads to the loss of humus and the formation of a red surface soil.

The cultivated examples of *terra rossa* are red to the surface and the general landscape is very like that of the corresponding areas in southern France and the coastal region of Algeria. Bare rock is a prominent feature and stony and bouldery slopes are common (Plate III, Fig. 2).

Along the Syrian coast north of the Homs–Tripoli gap there is a stretch of sand-dunes from which material has blown inland to give the soils a somewhat sandy surface. The following example of a *terra rossa* is from this area.

I.S. 16

4 miles south of Tartus and half a mile from shore. Elevation: 50 ft. Abundant annuals. Underlying rock: calcareous sandstone.

A_1	0–4 in.	Red-brown loam; porous, granular structure; few stones; abundant roots.
A_3	4–8 in.	Red-brown clay loam, fewer roots, somewhat stonier; fairly sharp transition to
B_2	8–20 in.	Reddish-brown clay loam, with abundant white mycelia of carbonate; small cloddy structure.
D	20 in.+	Decomposing rock.

The depth of soil over this area is quite variable with much bare rock exposed.

TABLE 7

Mechanical Analysis of Terra Rossa *Soil* (*I.S. 16*)

(Per cent. oven-dry soil)

Depth	*Coarse sand*	*Fine sand*	*Silt*	*Clay*	$CaCO_3$
0–4 in.	10·82	35·80	27·50	24·21	nil
4–8 in.	11·59	28·34	11·25	45·24	0·61
16–20 in.	10·71	27·99	12·00	43·43	3·20

Table 7 shows the mechanical analysis for this soil. There is a markedly higher fine sand and silt content in the surface soil, which is taken to indicate the contamination with wind-blown material from the shore. The calcium-carbonate content is low throughout.

The underlying decomposing rock is of a very sandy type and stained pink with iron oxides. It seems that this soil corresponds to the sandy red soils described by Reifenberg (1947) and Zohary (1947) as being formed over ancient (calcified) coastal sands and dunes. The boundary between the soil and the rock in the above case is very sharp and one would not expect such a high clay content in the residues from such a sandy rock. The soil layers are presumably derived from an ancient downwash from the mountains with more recent contamination from blown sand (cf. Rim, 1951).

An X-ray examination of the clay fraction of the above examples of *terra rossa* shows that they are essentially the same in composition, the constituent minerals being a kaolinoid of 'mellorsitic'* composition with some quartz, haematite, and mica. Differential thermal analysis agreed with this identification and indicated some amorphous material in addition. An electron micrograph is given in Plate IV, Fig. 4. Similar results have been reported by Kubiena (1948). Michaud *et al.* (1945) reported the presence of kaolinite and stressed the occurrence of attapulgite in the *terra rossa* they examined, but no further evidence for this has been reported. Hardon and Favejee (1939) identified metahalloysite in the red limestone soils of Java, and Bramao, Cady, and Hendricks (1950) refer briefly to halloysite being an important constituent of the Portuguese *terra rossa*. It would seem that one of the more hydrated or less well crystallized members of the kaolinoid group can be taken as fairly characteristic of these red limestone soils.

In general it appears that the processes leading to the formation of *terra rossa* are not dissimilar to those giving brown forest soils, and in fact Kubiena (1948) has suggested that they should be regarded as the end member of the sequence rendzina—brown forest soil—*terra rossa*. Decalcification proceeds from the beginning, and under forest the initial shallow soil would certainly be dark brown to black in colour. With continued development differentiation of a humose A_1 horizon with a crumbly or granular structure could take place, but under conditions of high base-status little or no differentiation of silica and sesquioxides would be expected once the soil had formed. Zohary (1947) recognized a decalcified *terra rossa* of which we think our woodland profile (I.S. 16A) is an earlier stage. The *terra rossa* described by Braun-Blanquet (1947) is also of this decalcified type, although not under woodland.

In various discussions of the origin of *terra rossa* much has been made of the apparent enrichment of the soil with sesquioxides and in particular iron oxide (cf. G. W. Robinson, 1949), and various suggestions such as volcanic dust, iron-rich solutions, and so on have been put forward in explanation. If, however, one examines the data given by Reifenberg (1947, p. 86) and Braun-Blanquet (1947) for the composition of a limestone and the overlying *terra rossa*, simple inspection indicates that there

* The fire-clay mineral of Brindley and Robinson (1947).

has actually been a relative loss of Fe_2O_3 during weathering if the *terra rossa* is assumed to be derived directly from the limestone. Using Merrill's method of calculating gains and losses on weathering and assuming alumina constant the relative loss of Fe_2O_3 is about 80 per cent. Taking silica as the constant constituent gives a loss of about the same value. In view of the fact that Merrill (1897, p. 232) gives an example showing similar losses it is surprising that no comment on this aspect appears to have been made by a soil worker.* This loss of iron from the weathering products would then be responsible for some of the red staining found lining cracks and fissures in the limestone. The transport of the iron oxide could readily be effected by the mechanism suggested by Reifenberg, i.e. peptization by small amounts of silica.

The real problem of these red soils on limestone would then appear to be more the form in which the iron occurs and not the amount present. Kubiena (1948) states that the iron oxide occurs in a highly dehydrated form and our X-ray data for the clay shows the presence of haematite, but not in very large amount (*c.* 5 per cent. of the 2 μ clay). It is probable that the oxide has in part formed small concretionary masses (Kubiena, 1948), in addition to tightly coating the sand grains. Differential thermal analysis suggests that part of the iron oxide is in a more or less amorphous state.

To the west of Homs a large area of brown soils on basalt flanks the northern side of the Homs–Tripoli gap and stretches westwards to within a few miles of the coast. The inland part is rough, hilly country, but near the coast to the south of Safita the land is smoother and the extensive Plain of Akkar is largely underlaid by basalt. The soils are very fertile and even the boulder-strewn land near Homs is well cultivated, much being under cereals.

In contrast to the *terra rossa* the dark brown colour of the basaltic soils looks almost black, and this darkening is locally intensified by an abundance of black oxides in the coarser fractions. The soils seem to be invariably shallow, even on areas of flat relief, and there is little evidence of profile development. The following profile is representative.

I.S. 15

8 miles west of Homs. Strongly rolling country; site on gentle slope. Elevation: 1,200 ft. Vegetation: grasses, clover, annuals.

A_p	0–9 in.	Dark brown (7·5 YR 3/2) clay, cloddy; abundant roots and earthworms; very stony, merges into
B	9–22 in.	Dark reddish-brown (5 YR 3/3) clay, cloddy; few roots, earthworms present; mass of boulders at 18 in. with clay between.
D	22 in.+	Basalt.

Zohary (1947) has described similar soils from the J. Druze district, including some that are calcareous.

In the section on geology mention has been made of the variation in crystallinity of the basalt rock, and this variability is well expressed in

* C. G. Morgan and S. S. Obenshain (*Proc. Soil Sci. Soc. Amer.* 1942, **7**, 441), in a study of three limestone soils from the grey-brown podzolic region of the United States, report between 97 and 213 per cent. Fe_2O_3 saved in the weathering of the bedrock to form soil parent material.

the soils. The rock underlying the above soil (I.S. 15) is a typical olivine basalt with phenocrysts of olivine in a holocrystalline groundmass composed of abundant augite, calcic plagioclase (labradorite), olivine, magnetite, and calcite, the latter also occurring in vesicles. In contrast to this is the rock underlying profiles (e.g. I.S. 17) collected on the Plain of Akkar, near Safita. This basalt is a merocrystalline rock with conspicuous phenocrysts of olivine in a matrix composed of a brownish glass showing a well-developed perlitic structure and enclosing feldspar (labradorite) laths with accessory brown pseudomorphs (? iddingsite) after an original feromagnesian mineral. A micrometric analysis of the *groundmass* gave the following approximate modal composition (volume per cent.): glass 72, feldspar 22, brown pseudomorphs 6.

TABLE 8

Exchangeable Cations in Brown Soils on Basalt

(m.eq. 100 g. oven-dry soil)

Depth	Ca	Mg	Sr	Na	K	Mn	Σ	*pH*
				I.S. 15				
0–3 in.	19·6	8·5	0·058	0·4	0·4	0·1	29·1	6·7
6–9 in.	17·7	9·2	0·067	0·4	0·2	0·05	27·7	6·5
9–12 in.	19·7	10·7	0·079	0·5	0·2	0·03	31·2	6·7
22 in.+	20·7	7·1	0·075	0·5	0·2	0·02	28·6	6·9
				I.S. 17				
0–4 in.	24·8	22·5	0·1	0·9	0·7	0·02	49·0	7·0
4–8 in.	38·8	25·1	0·1	0·6	0·4	0·06	65·0	6·5
8–12 in.	30·3	26·9	0·12	0·6	0·3	0·07	58·2	6·8
13–15 in.	41·2	35·8	0·17	0·7	0·3	0·03	78·1	6·9

This difference between the two parent rocks is very strikingly reflected in the chemical properties of the soils and the composition of the clay fraction. Table 8 shows the exchangeable base data for the two soil types. In the case of I.S. 15, derived from the holocrystalline rock, the calcium/magnesium ratio is roughly what one might expect from a basic igneous rock, whereas the ratio in I.S. 17 from the glassy rock is more like that from an ultrabasic material, e.g. picrite (cf. Mitchell, 1937). The Ca/Sr and other ratios are also markedly different for the two soils. There is a sharp rise in the content of bases in the lowest layer of I.S. 17, but there is no significant change in the ratios of the individual cations.

In I.S. 15 (crystalline basalt) the dominant clay mineral is a kaolinoid approximating to halloysite, but in the fine material from just above the weathered rock there is also a vermiculite-like material which decreases in amount in the upper soil layers. Goethite is also indicated by X-ray examination. Differential thermal analysis shows a considerable amount of amorphous material which is removed from the clay by sodium-hydrosulphite treatment and therefore probably consists to some extent of iron oxides.

In the soil from the glassy basalt (I.S. 17) the dominant clay mineral is a montmorillonoid—probably a beidellite, with a small amount of an unidentified mineral and goethite. Differential thermal analysis also

indicates a montmorillonoid and shows in addition amorphous oxides. This association of a montmorillonoid with a glassy basic rock is a characteristic feature of the occurrences of this mineral group (cf. Ross and Hendricks, 1945).

Shadowed electron micrographs of the untreated clay from the basalt soils (Plate IV, Fig. 5) shows large clumps of material like cotton-wool, only a few particles showing sharp outlines. Treatment with hydrosulphite breaks down some of the aggregates and further treatment with acid oxalate cleans up almost all of these and leaves small and rather thin plates (Plate IV, Fig. 6). In I.S. 15 the halloysite plates are somewhat thicker and better defined than the beidellite of I.S. 17. The pretreatment, of course, may have affected the less stable beidellite to some extent.

These differences between the clays derived by the weathering of the basalts is to some extent in contrast to the findings of Hosking (1940) for Australian conditions, where under a climate with 'protracted drought periods montmorillonite is the characteristic mineral'. The Homs region enjoys a Mediterranean steppe-like climate with a very dry summer and the soils are near neutral in reaction—just those conditions one would expect to yield montmorillonite. Ross and Hendricks (1945) have pointed out that differences in the weathering products of diabase in the eastern United States must be ascribed to differences in the rock and not to climate, and presumably the same is true for these Syrian soils. It would be interesting to know the clay-mineral composition of the basalt soils of the drier regions of the Hauran and J. Druze to the south.

Reference has been made in the discussion of *terra rossa* to the apparent considerable loss of Fe_2O_3 in the weathering of the limestone. Calculation of Reifenberg's analyses (1947, p. 86) for the basalt and its overlying soil shows a very different picture—only 8 per cent. of the iron oxide has been lost as against 78 per cent. in the *terra rossa*. This result, however, takes no account of the amount of magnetite present and it can reasonably be assumed that this form would not be very mobile. Examination of the sands from our samples of basalt soils shows a rather high proportion of black oxides and the coarse-sand grade shows a number of spherical iron-oxide concretions.

The coastal region of the Lebanon is very narrow and the mountains rise steeply to over 10,000 feet, displaying an excellent vertical zonation, similar to that seen in southern France and in Algeria. The *terra rossa* gives way rather sharply to brown forest soils with rising elevation and these in turn to podzolic soils as the land levels out towards the summits. There is, of course, some variation in parent material and this also affects the soils considerably. Cultivation on terraces extends high up the mountains and some excellent afforestation is being carried out. The pine forests we saw appeared to be mainly on the brown forest and podzolic types of soils.

Summary

An account is given of the main soil groups occurring in Syria, together with chemical and clay mineral data. The main soil groups

recognized are, in the desert, desert soils and solonchakous soils, with undeveloped soils on alluvium; in the steppe and desertic steppe, grey and red-brown soils corresponding in some features to the Russian sierozem and possibly to reddish chestnut soils; in the Mediterranean zone *terra rossa* and brown soils on basalt, with gley soils on alluvial flats. The effect of parent material is well marked in all the zones. The occurrence of attapulgite in some of the desert and steppe soils is reported.

Acknowledgements

I have to thank Mr. W. Whalley of the Iraq Petroleum Company for information on the desert crust and also for obtaining additional profiles of basalt soils. The data for water-soluble salts were kindly provided by the Research Station of the Anglo-Iranian Oil Company. My colleagues Dr. D. M. C. MacEwan and Mr. K. Norrish very kindly assisted with the interpretation of X-ray data and Mr. I. Stephen carried out the petrographic analysis of the samples of basalt: Mr. H. Nixon made the very fine electron micrographs: to them also I would express my thanks.

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POSTSCRIPT

A Note on the Crook-ard in the Middle East

The agricultural implements used by the peasants throughout the Middle East are extremely primitive in type, as can be seen by comparing the illustrations of ploughs in Plate VI, Figs. 1 and 2, with the drawings given by E. C. Curwen in his *Plough and Pasture* (1946).

The construction of the plough is simple and the implement very light although in appearance awkward and roughly finished. It possesses no wheels or coulter and the ploughshare in its simplest form is a pointed spade-shaped piece of iron (Plate V, Fig. 1), there being no mould-board. A slightly more advanced form with 'ears' is shown in Plate III, Fig. 1. The shaft generally consists of at least two pieces roughly joined together and tied with rope, and there is usually only one stilt. An exception to this is seen in Plate V, Fig. 2, where a V-shaped double stilt is used. Traction is provided by oxen, ass, or camel, and the light construction makes the plough readily transportable.

This type of plough does little more than scratch the surface of the soil, the furrows not exceeding 4–6 in. in depth, but under the climatic conditions prevailing it is probable that little more is required. There is no deep leaching of plant nutrients and little organic matter to bury. The rough, cloddy, surface that is produced will reduce erosion and conserve moisture during fallow periods. Sowing takes place directly on the ploughed land; harrows and rollers are apparently unknown. The crops would commonly appear to be very weedy, for many of the weeds are deep rooting and the ploughing does little to destroy them.

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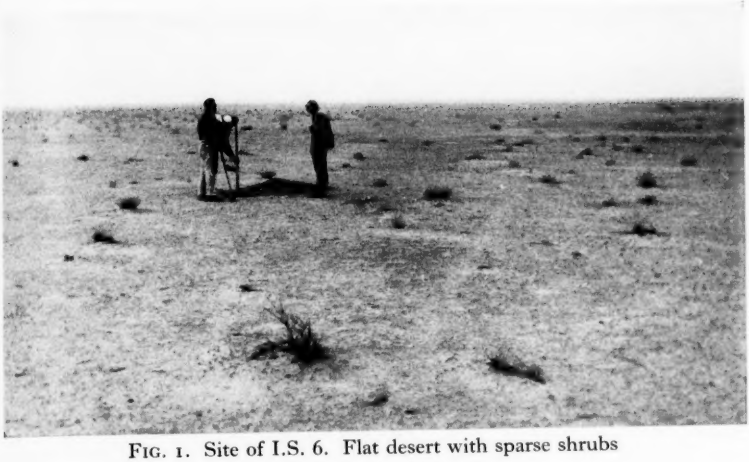

FIG. 1. Site of I.S. 6. Flat desert with sparse shrubs

FIG. 2. Rolling Downland in Desertic Steppe near T_4

A. MUIR—NOTES ON SYRIAN SOILS—PLATE I

FIG. 1. Red-brown steppe soil (e.g. I.S. 13) on hard limestone (Turonian)

FIG. 2. Spring cultivation of red-brown steppe soil east of Homs. Note jointed shaft of plough

FIG. 1. Typical Middle-East ploughshare, near Homs

FIG. 2. Near Safita on *Terra Rossa*. Strong sheet erosion in foreground. Partially terraced fields

A. MUIR—NOTES ON SYRIAN SOILS—PLATE III

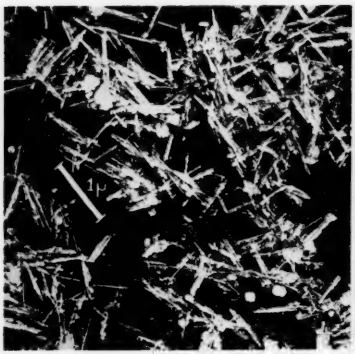

FIG. 1. I.S. 10 (7–12 in.)
< 2 μ clay
(untreated)
Predominantly attapulgite

FIG. 2. I.S. 7 (20–24 in.)
< 2 μ clay
(untreated)
Predominantly attapulgite

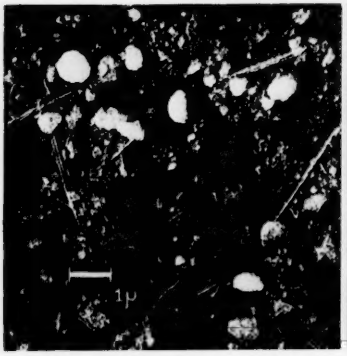

FIG. 3. I.S. 13 (22–26 in.)
< 2 μ clay
(oxalate treated)
Kaolinite, mica, and attapulgite

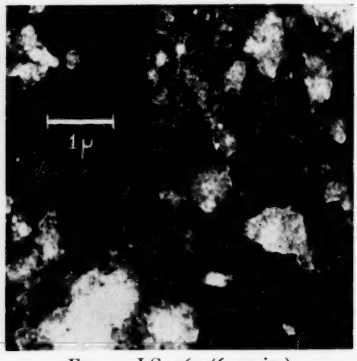

FIG. 4. I.S. 16A (6–12 in.)
< 2 μ clay
(oxalate treated)
'Mellorsite' with some quartz

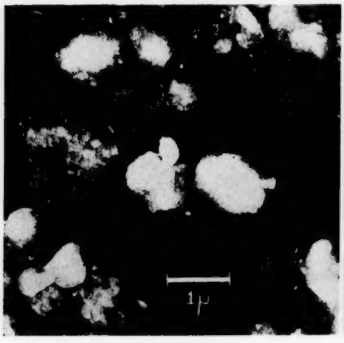

FIG. 5. I.S. 17 (8–12 in.)
< 2 μ clay
(untreated)
Beidellite aggregated with sesquioxides

FIG. 6. I.S. 17 (8–12 in.)
< 2 μ clay
(oxalate treated)
Beidillite

A. MUIR—NOTES ON SYRIAN SOILS—PLATE IV

FIG. 1. Two-stilt crook-ard. Labhari Valley, Khuzistan, Persia

FIG. 2. Single-stilt crook-ard, Homs district, Syria

CHARACTERIZATION OF BELGIAN SEA-POLDER SOILS BY THE CLAY FRACTION AND CATION-EXCHANGE CAPACITY

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THE Belgian sea polders were the first to be studied systematically in the Belgian soil survey (research subsidized by I.R.S.I.A.).† This was done by the Centre at Ghent. The characterization of the soil types in this survey includes the mechanical composition of the soil. Clay sediments of different age are distinguished in the Belgian sea polders. The deposition of the oldest clay, which is called the old polder-clay, started after the second Dunkirk transgression (fourth century). The area so covered is called the old sea-polder region and extends over more than 22,000 hectares. It was protected against new inundations in the tenth century by the construction of a dike, the oldest dike in the country. During the inundations of the third Dunkirk transgression (ninth century) a large area of the non-protected old polder-clay was covered with a new clay layer. This area is called the covered region of the sea polders and extends over more than 30,000 hectares.

In both regions two soil series may be clearly distinguished: the basin soils and the creek soils. We have tried to characterize the different polder-clays by the percentage of clay (0–2 μ) in the clay and silt (0–20 μ) fraction. Since the method for the determination of the 0–2 μ clay and of the 0–20 μ fraction was changed about a year after the study was started, the different results obtained on the same polder-clay as well as the results of the mechanical analyses of the different polder-clays will be discussed in this paper.

Mechanical Analysis

Because a quick method to work up a large number of samples was needed, the pipette method of Khön (1928) was used. Three different procedures were used in preparing the soil samples.

1. *Preparation by filtration with 'Jena-Filter 5' and* NH_4OH *as diffusing agent*

The pulverized and air-dried soil sample is placed in a beaker of 800 ml., and treated with 100 ml. of H_2O_2 (100 vol.) to destroy the organic matter. The following day 100 ml. of 0·2N HCl and an excess of 0·4 ml. of 12N HCl for each per cent. of $CaCO_3$ in the air-dried soil are added. The whole is boiled until no more CO_2 escapes. The suspension is filtered under vacuum on a Jena Filter '25 G 5 auf 3' (micropores

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1 to 1·5μ) and washed twice with 250 ml. of distilled water, stirring the material thoroughly between each filtration. After the filter with the residue has been dried at 105° C. the latter is pulverized in a porcelain mortar. Then 10 g. of pulverized soil is weighed and sieved under water, through a sieve of 50μ. The fraction greater than 50μ is dried and sieved with a Rotap.

If necessary, the suspension with particles less than 50μ is reduced to a volume of 500 ml., and 50 ml. of 10 per cent. NH_4OH solution is added as dispersing agent. Finally, the suspension is shaken for 24 hours and the volume made up to 1 litre. According to Stokes's law 10 ml. containing the clay and silt fraction is pipetted after 4 min. 53 sec. at 18° C. at a depth of 10 cm., and 10 ml. containing only the clay fraction after a sedimentation time of 8 hrs. 10 min. at 18° C.

About 300 soil samples from 70 profiles of the old polder region were analysed in this manner. The profiles included both creek soils and basin soils.

2. *Preparation by filtration with 'vegetal-paper' and* NH_4OH *as diffusing agent*

Since new filter plates ('Jena 5 auf 3') were not available, it was necessary to use Jena filters G 4 (micropores between 5 and 15μ). To be useful for clay filtration, the filter plates had to be covered with a membrane. A special kind of paper, called 'vegetal paper', was used for this purpose. This was the only modification of the first treatment.

About 200 samples from 30 profiles of the covered polder region were studied by this modified procedure. The samples included both creek and basin soils.

3. *Preparation by use of the siphon method and a mixture of* $Na_2C_2O_4$ *and* Na_2CO_3 *as diffusing agent*

A 20-g. sample of pulverized soil is put into an 800-ml. beaker, and 100 ml. of H_2O_2 (100 vol.) is added. The next day H_2O_2 is added again, the contents are heated on a steam bath, and finally boiled for at least 5 minutes until all the H_2O_2 is consumed. After cooling, 100 ml. of 0·2N HCl is added with an excess of 0·33 ml. of 12N HCl for each per cent. of $CaCO_3$ in the soil on the dry-weight basis. Then 400 ml. of distilled water is added and allowed to stand overnight. The following day the clear supernatant solution is carefully siphoned off. About 700 ml. of distilled water is added to the beaker, the contents are stirred, and the soil is allowed to settle.

The next day the supernatant solution is siphoned again, about 700 ml. of distilled water is added, and the contents are stirred. The following day the supernatant solution is siphoned a last time and the soil is sieved under water through a sieve of 50μ. For the suspension containing the particles less than 50μ, 50 ml. of a solution containing 13·399 g. of $Na_2C_2O_4$ and 2·12 g. of Na_2CO_3 per litre is added and the volume is made up to 1 litre with distilled water. Thus we have a concentration of 0·01N $Na_2C_2O_4$ and of 0·002N Na_2CO_3 in the clay suspension.

After vigorous shaking, the suspension is pipetted as indicated for the first treatment. Each time 10 ml. are pipetted a correction of $\pm 7{\cdot}75$ mg. for the dispersing liquid is necessary. The exact amount of correction is determined by drying 10 ml. of the dispersing liquid.

About 200 samples from 30 profiles of the old polder region and about 500 samples from 90 profiles of the covered sea polders were studied in this manner.

Results

The results for each horizon of eight profiles as obtained by the three methods of soil-sample preparation are presented in Tables 1 and 2. The data are representative of those obtained for a large number of profiles.

TABLE 1

Percentage of Clay (0–2 μ) in the 0–20 μ Fraction for Basin and Creek Soils as determined by Different Treatments of the Soil Sample

Clay of old sea polders					*Clay of covered sea polders*				
Creek soil: Profile 51 E/33 Filter method: 'Jena 25 G 5 auf 3', NH_4OH as dispersing agent					*Creek soil*: Profile 51 W/21 Filter method: 'Vegetal paper', NH_4OH as dispersing agent				
Horizons depth	$< 2\ \mu$	$< 20\ \mu$	*Clay in 0–20 μ fraction*	*Average*	*Horizons depth*	$< 2\ \mu$	$< 20\ \mu$	*Clay in 0–20 μ fraction*	*Average*
(*cm.*)	%	%	%	%	(*cm.*)	%	%	%	%
0–12	13·0	26·3	49·4	49·2	0–20	22·1	51·3	43·1	43·6
12–29	14·3	30·9	46·2		20–42	27·2	61·1	44·5	
29–45	8·9	18·9	47·1		42–64	20·0	43·2	48·6	
45–67	8·5	17·6	48·3		64–89	17·3	43·7	39·6	
67–99	7·6	13·5	56·3		89–150	10·0	23·0	43·5	
99–124	7·2	15·1	47·7		..	..	..	..	..
Basin soil: Profile 51 W/53 Filter method: 'Jena 25 G 5 auf 3', NH_4OH as dispersing agent					*Basin soil*: Profile 51 E/14 Filter method: 'Vegetal paper', NH_4OH as dispersing agent				
Horizons depth	$< 2\ \mu$	$< 20\ \mu$	*Clay in 0–20 μ fraction*	*Average*	*Horizons depth*	$< 2\ \mu$	$< 20\ \mu$	*Clay in 0–20 μ fraction*	*Average*
(*cm.*)	%	%	%	%	(*cm.*)	%	%	%	%
0–15	37·5	72·6	51·6	48·0	0–27	35·1	85·5	41·1	43·3
15–65	36·0	71·9	50·0		27–56	38·8	90·2	43·0	
65–84	36·1	73·1	49·4		56–101	38·5	86·5	44·5	
84–123	30·8	69·9	44·1		101–131	38·5	86·7	44·4	
123–135	36·6	80·1	44·9		..	..	..		..

It is noted that the values for 0–2 μ clay obtained by filtration with the 'vegetal paper' are slightly lower than those obtained by filtration with the 'Jena filters 5'. This difference is attributed to the nature of the filter and not to the method of preparing the soil samples. One of the outstanding features shown by the data is that the per cent. of 0–2 μ clay in the 0–20 μ fraction in the different horizons of the various soil profiles does not fluctuate to any significant degree. This holds for each of the three methods of soil-sample preparation and for both the creek and the

basin soils. The average value of the different horizons of a profile is truly a representative value for the clay layer of that profile. Thus the average values are representative of the clay layers of both of the creek and basin soils in each of the two polder regions.

TABLE 2

Percentage of Clay (0–2 μ) in the 0–20 μ Fraction for Basin and Creek Soils by the Siphon Method using $Na_2C_2O_4$ *and* Na_2CO_3 *as Dispersing Agent*

Clay of old sea polders					*Clay of covered sea polders*				
Creek soil: Profile 51 W/12					*Creek soil*: Profile 36 W/22				
Horizons depth	< 2 μ	< 20 μ	*Clay in 0–20 μ fraction*	*Average*	*Horizons depth*	< 2 μ	< 20 μ	*Clay in 0–20 μ fraction*	*Average*
(*cm.*)	%	%	%	%	(*cm.*)	%	%	%	%
0–16	17·8	25·9	68·7	67·7	0–17	32·8	55·0	59·6	67·3
16–29	24·0	36·9	65·0		17–31	22·7	34·8	65·2	
29–58	16·2	23·7	68·0		31–61	13·0	17·6	73·9	
58–76	7·5	11·3	66·4		62–85	10·9	15·5	70·3	
76–86	15·0	21·8	68·8		85–110	16·9	24·4	69·3	
86–132	7·4	10·7	69·2		110–135	9·4	14·4	65·3	
Basin soil: Profile 50 E/49					*Basin soil*: Profile 36 E/3				
Horizons depth	< 2 μ	< 20 μ	*Clay in 0–20 μ fraction*	*Average*	*Horizons depth*	< 2 μ	< 20 μ	*Clay in 0–20 μ fraction*	*Average*
(*cm.*)	%	%	%	%	(*cm.*)	%	%	%	%
0–16	32·6	56·0	58·2	66·1	0–18	32·0	49·6	64·5	68·1
16–28	45·0	66·2	67·9		18–35	42·5	61·8	68·8	
28–44	54·3	76·7	70·8		35–52	48·1	73·2	65·7	
44–65	53·4	77·0	69·4		52–72	29·2	41·7	70·0	
65–90	52·0	80·7	64·4		72–110	14·4	20·1	71·6	

Reproducible results can be obtained readily with any of the three methods of sample preparation and with both dispersing agents. A markedly larger percentage of 0–2 μ clay was obtained, however, with the dispersing agent consisting of a mixture of $Na_2C_2O_4$ and Na_2CO_3 than with NH_4OH. Therefore, when the characteristics of a clay sediment are determined it is important to mention the dispersing agent used in the mechanical analysis of the soil profiles. The importance of dispersing agents was also pointed out by Hooghoudt (1945).

General averages of more than 1,000 mechanical analyses, calculated as shown in Tables 1 and 2, are presented in Table 3. The average values for 221 profiles are classified according to the kind of clay, the soil series and vegetation, and the kind of dispersing agent used.

The results show that:

1. The difference in age and in mineralogical composition of the clays, as shown by differences in exchange capacity in Table 3 and elsewhere (Leenheer *et al.*, 1950), is not reflected in the mechanical composition of the two polder-clay layers as determined by mechanical analysis.

2. The 0–2 μ clay content in the 0–20 μ fraction is essentially the same for both the creek and the basin soil series. This was shown regardless of the dispersing agent used.
3. The actual amount of 0–2 μ clay in the 0–20 μ fraction in heavy soils such as the sea-polder soils is dependent on the dispersing agent used.

TABLE 3

Percentage of 0–2 μ Clay in and Exchange Capacity of the 0–20 μ Fraction in Belgian Sea-polder Soils

Old sea-polder soils	Siphon method using $Na_2C_2O_4 + Na_2CO_3$ as dispersing agent		Filter method: 'Jena G 5', using NH_4OH as dispersing agent		
	Number of profiles	*Average 0–2 μ clay, %*	*Number of profiles*	*Average 0–2 μ clay, %*	*Average exchange capacity, m.e. per 100 g.**
Meadow on basin soil	14	65·8	25	48·25	44·4
Ploughed land on basin soil	5	65·9	4	49·6	45·0
Meadow on creek soil	1	66·9	10	48·9	44·4
Ploughed land on creek soil	14	67·9	29	49·6	44·4
Total numbers of profiles	34		68		
Average values		66·7		49·1	44·7

Covered sea-polder soils	Siphon method using $Na_2C_2O_4 + Na_2CO_3$ as dispersing agent		Filter method: 'Vegetal paper', using NH_4OH as dispersing agent		
	Number of profiles	*Average 0–20 μ clay, %*	*Number of profiles*	*Average 0–20 μ clay, %*	*Average exchange capacity, m.e. per 100 g.**
Meadow on basin soil	27	65·2	10	42·0	37·4
Ploughed land on basin soil	8	64·3	2	42·2	37·7
Meadow on creek soil	1	65·2	6	43·9	37·7
Ploughed land on creek soil	54	66·2	11	43·7	37·8
Total numbers of profiles	90		29		
Average values		65·8		42·1	37·6

* The exchange capacity was determined by replacement of the cations with 0·1 N $BaCl_2$ according to the method of Schachtschabel.

In view of the suggestion of Hooghoudt (1945) that a mixture of $Na_2C_2O_4$ and Na_2CO_3 makes a desirable dispersing agent in comparison to many he has studied, the subject was not pursued further, though it is recognized that it merits further investigation.

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THE INFLUENCE OF GEOPHYSICAL PROCESSES ON THE STRATIFICATION OF SANDY SOILS

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Introduction

MANY of the coastal plains bordering on the Mediterranean shores, such as those of Algeria and other countries, are covered by deep layers of red sandy soils which are always combined with other sandy deposits. They seem to be most predominant along the eastern coast of the Mediterranean. Here the parent material for these formations is being amply supplied by sea currents and winds from the Sinai coast and the desert of the isthmus (1). Such red sandy soils make up most of the citrus area in Israel. They are sometimes underlaid by a discontinuous horizon of hard-pan, called Nazzaz, which often presents an agricultural problem and has, therefore, been the subject of repeated investigations (2, 3, 4, 5). The development of these clay patches could not, however, be understood pedogenetically. Likewise a supposed formation of the red sandy soils themselves from the always associated calcareous sandstone could not be proved. The latter, where it covers the surface, weathers to another type of soil, the grey Kurkar soil (5, 6).

Attempts to classify these various layers on a chronological, geological basis were not successful (7, 8, 9). It was known that all these various, always associated formations originated from dune sand, but it could not be understood why the sand should have become converted into such fundamentally different products. Likening the formation of red sandy soils to that of laterites, one hypothesis postulated sudden, extreme cyclic alterations of climate in past geological periods. Such assumptions, however, failed to be supported by other evidence (9, 10, 11, 12). An alternative theory (9, 13) assumed pluvial floods to have washed down *terra rossa* from the mountainous hinterland. Alluvial material would have thereby become incorporated into the coastal sands, thus causing the typical texture and colour of the red sandy soils. This theory does not take account of the topographical conditions—a wide, low-lying belt, entirely free of such formations, stretching between the mountains and the coastal dunes. As a third alternative Vroman (20) suggested that the differences of the various sandy deposits might be the result of ground water having penetrated the sand masses at different levels in the past.

The vagueness of all these hypotheses, as well as the opposing evidence, led Reifenberg to the conclusion that the red sandy soils, although often found in a fossil state, were not only products of distant geological periods, but were also being formed continually by pedogenic processes under present conditions (5). The mechanism of formation and the peculiar structure of the resulting soil became understood after recent studies on the supply of the parent material and on the sorting it undergoes before being permanently deposited (1, 14, 15).

Mechanical Selection Processes during the Accumulation of Soil Material

Where the parent material of a soil is not solid rock, but non-cohesive, constantly shifting aeolian or alluvial material, mechanical sorting and grading of the various minerals is bound to take place prior to and during the development of the soil. Under the influence of surface conditions, topography, and climatic factors, distinct layers are likely to be built up on differently situated places by selective retention of specific minerals. Such selection processes are comparatively easily studied in the case of sand-dunes, whose accessibility and bareness facilitate observation and experimentation. Here selection processes are most significant, since wide areas are being affected at one and the same time, while similar processes taking place under the force of flowing water—along water-courses, for instance—can only cause linear effects.

Observations in Israel's coastal dune belt revealed the existence of a sorting cycle. Entirely differently composed sand mixtures are being retained on dune slopes facing the wind and are left behind on the wind-shaded slopes. As the dunes shift and grow while these different deposits are being laid down on opposite slopes, straight-bordered sediment layers ensue, whose exact shape and composition depend on the sand-supply rate and its relation to the velocity and the height growth of the dunes.

The sorting processes and their effect are not all observable on the surface, which is usually covered by unsorted transitional material. The most effective stage of the sorting takes place underneath the sliding sand sheets on the slip-slopes. Such slopes invariably develop on the wind-shadowed parts of the dunes. Here the sand becomes piled up until its natural angle of repose is reached and until it starts to slide down under the force of gravity. During this motion the smaller and denser grains penetrate into the stationary layers beneath, while the large and flat ones float down with the top layer. The slip-slopes build forward against the undercutting tendency of a wind vortex in front of it, by which surface material is continually being removed. This material, which is driven on to the next dune, is therefore of a textural and mineralogical composition complementary to the material remaining underneath the slip-slope.

As this sand mixture ascends the wind-swept slope of the next dune, sorting in the opposite direction is brought about. Like all wind-swept sand surfaces, these slopes are covered by ripple marks. It is shown in a separate paper that ripple marks are directly connected with the heterogenity of the passing sand, whereby the various fractions of the sand become separated on the surface. (Uniform sand never forms ripple marks.) When sand accumulates on the wind-swept surface with the ripples passing over it, each ripple leaves a thin, straight lamella of sorted minerals. Thus a closely packed, laminated deposit is built up. Paradoxically it consists in its main part not of those grains which occupy the ripple troughs, but of those which always make up the ripple ridges. The latter are observed to be mostly coarse, non-bouncing grains and

happen to be identical with those grains which fail to be incorporated into the slip-slope deposits just described.

Aerodynamical studies (15, 16, 17, 21, 22) showed that this identity is not purely incidental, but that it is the consequence of a tendency of wind-transported sand-mixtures to converge towards certain more wind-stable compositions. Thus every time the sand's composition becomes changed due to outside factors, such as the slip-slope sorting, the original composition tends to be restored by the wind on the wind-exposed

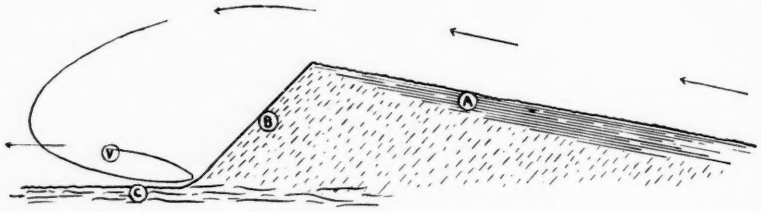

FIG. 1

slopes of the following dunes. This, naturally, is achieved by depositing those fractions which are complementary to the ones retained underneath the slip-slopes.

The efficiency of slip-slope sorting—which is a measure of the total sorting taking place—is roughly proportional to the slip-slope's height and to the amount of material deposited in relation to the amount passed on. Fast-moving or growing dunes sort less efficiently than almost stationary ones.

Apart from the described formation of twin deposits due to mechanical and aerodynamical sorting, layers also result from the washing-down of easily suspendible particles into the wind holes that occupy the interspaces between the individual dunes. During the rainy season puddles form in these pans, which are devoid of drainage outlets. They leave impervious layers of clay material on drying out. These alluvial patches become, in due course, buried underneath the advancing slip-slope of the windward dune.

In view of the existence of various dune types forming irregular patterns near the shore and near the opposite fringe, a description of the ensuing arrangement of layers cannot apply generally. It might be shown schematically as in Fig. 1. The deposit accumulating under the slip-slope *B* was called encroachment-deposit by Bagnold (22), and the one under the rippled surface *A*, accretion-deposit. *C* is the alluvial material whose depth usually does not exceed 1 metre, while the depth of *B* corresponds to the height of the slip-slope and may easily exceed several dozen metres. The vortex *V* was found to lie obliquely—almost flat—removing the material from the foot of the slip-slope sidewards.

Partial erosion and re-formation of dunes out of locally eroded material are likely to cause thinner layers and more complicated arrangements.

The Mineralogical Composition of the Various Layers and the Subsequent Changes due to Weathering

The mineralogical composition of the raw material—the sand supplied by the long-shore current off Israel's coast—is on the average uniform all along the coast. The sand has become well graded by the long transport it underwent—from the Sinai coast northwards—which means that the ratios between the diameters of grains having different physical properties are fairly constant. (The relative *quantities* of the various fractions are, however, not constant, varying according to the local conditions of deposition.)

TABLE 1

Composition of Various Sand and Sandy Soil Layers (from Holon and Bnei Braq, near Tel-Aviv)

	Sand accretion layer	*Sand encroachment layer*	*Alluvial material between dunes*	*Calcareous sandstone*	*Red sandy soil*	*Pan (Nazzaz)*
Coarse sand, %	13·5	2·3	4·2	..	7·1	2·1
(its $CaCO_3$ content), %	(85)	(15)	(30)	..	(0·1)	(0)
Fine sand, %	80·1	86·5	84·5	..	80·5	69·2
Silt, %	6·1	9·6	8·7	..	5·2	7·4
Clay, %	0·3	0·5	3·6	..	7·2	20·3
Total $CaCO_3$, %	20·6	3·2	1·8	41·1	0·8	0·03
Dense minerals, %	5·3	7·0	6·8	4·5	7·2	8·2
(fraction of dense mineral grains larger than 0·15 mm.) approx. %	(2)	(1)	(1)	(3)	(2)	(2)
Relative frequency of grains of dense minerals (in brackets: number of grains larger than 0·15 mm.)						
Opaque (magnetite)	41 (20)	43 (6)	46 (4)	40 (21)	60 (6)	56 (4)
Tourmaline	2 (0)	1 (0)	..	..	..	..
Zirkon	4 (2)	3 (0)	3 (0)	7 (2)	3 (0)	5 (0)
Garnet	2 (0)	2 (0)	1 (1)	1 (0)	1 (0)	2 (0)
Rutile	4 (3)	1 (0)	1 (0)	6 (4)	2 (0)	5 (1)
Titanite	..	2 (0)	..	1 (1)	..	..
Staurolite	1 (1)	..	..	..	1 (0)	..
Kyanite	1 (0)	..	1 (0)	2 (1)	..	2 (0)
Epidote	11 (6)	15 (3)	15 (1)	18 (2)	17 (2)	16 (1)
Hornblende	20 (11)	23 (3)	17 (2)	22 (13)	15 (2)	14 (2)
Augite	14 (8)	9 (1)	6 (1)	3 (2)	1 (1)	..

In a well-graded mixture only such grains will be found together that behave similarly towards the coastal transport agencies. It can be seen that, as a first approximation, size and density of the grains counterbalance each other. Where larger grains are associated with smaller ones in a natural sand-mixture, the former are always those of the lowest density and vice versa. This scheme is likely to be upset only by fragile minerals, which may render a finer fraction than expected according to the grading scheme, after having become broken or worn during the transport.

The latter anomaly is observed to happen in the case of the fragments of thin shells of invertebrates which consist of aragonite. The distribution of this mineral is, moreover, influenced by varying, unpredictable

local biological conditions. In spite of this, aragonite always constitutes the characteristic part of the coarse fraction which, as was described, rides on the surface of the sliding sand sheets down the slip-slopes and forms thereafter the accretion-deposits.

The grains of the denser mineral measure diametrically about the third of the quartz grains, between which they are interspersed, constituting approximately 4–6 per cent. by weight of the whole mixture. They are predominantly magnetite, hornblende, epidote, augite, rutile, zirkon, and garnet, as a rule found in relative frequencies of 50:25:15:5:5:3:1, respectively (1, 14, 15, 20). These are the minerals that concentrate underneath the surface layer of the slip-slope. Their concentration there rises often to twice the average amount. At the same time these deposits are found to be almost deficient of $CaCO_3$ (aragonite). (See Table 1.)

The main body of all deposits consists of rounded quartz grains with some felspar, mica, calcite, and occasionally flint grains. The further development of the deposit, however, is determined by the ratio between the accessory minerals (the finely grained, dense minerals) on the one hand and the large ones ($CaCO_3$) on the other. In the presence of moisture these two groups of minerals react differently and behave antagonistically towards the other grains in the deposit. The $CaCO_3$ may be dissolved and transported in that state, while the dense minerals can only be hydrolysed. The resulting hydrated sesquioxides may be transported only if a peptizing agent is present. These two processes—transport of $CaCO_3$ and mobilization of sesquioxides—are of alternative nature, as both the $CaCO_3$ and the peptized sesquioxides tend to cement the other grains, thereby preventing each other from taking part in further chemical reactions.

Sand samples taken from more than half a metre's depth were invariably found to be wet, irrespective of the season of the year (under the condition, of course, that the respective deposit was older than the current summer season). In view of the total absence of evaporation from the surface of loose sand deposits, the movement of moisture is—in spite of the hot local climate—predominantly downwards and soluble components are leached out. Thus the loose encroachment deposits tend to lose the small amount of finely powdered calcium carbonate, which had a chance to penetrate during their formation.

Viewed under the microscope, such samples show that limonitic products of hydrolysis from dense materials—mostly iron ores—coat the quartz grains, whereby the sand as a whole assumes a yellow or reddish appearance. These hydrates of iron oxide are mainly derived from the tiny magnetite particles, which even themselves are seen to adhere to the surface of the quartz grains.

The capability of silica in the colloidal state to peptize iron oxides was demonstrated by Reifenberg (24) and may explain the affinity of limonite to the quartz surface and their mobility in its proximity. The amount of soluble and colloidal silica in such soil-like sands is found to be above the average for local soils (approx. 0·01 per cent.).

The well-packed, $CaCO_3$-rich accretion deposits, on the other hand,

are not liable to lose their $CaCO_3$ by leaching, because of the larger size of the $CaCO_3$ grains and the lower percolation rate through these deposits. Furthermore, water movement seems to be balanced here due to the possibility of moisture being drawn upwards by capillary action and evaporation on the surface. Quite apart from the above-mentioned reasons both hydrolysis and peptization of magnetite and other minerals are impeded in the accretion deposits because of their bigger grain-size. Thus all grains soon become incrusted by $CaCO_3$ and are, in the course of time, converted into laminated calcareous sandstones, fully cemented by calcium carbonate.

The Maturing of Red Sandy Soils

The sorting processes, described above, explain the origin of red sandy soils.

As artifacts have been found embedded within layers already in an advanced state of cementation (or hydrolysis), the chemical changes can be approximately timed (11, 27). Not very deep sampling of sand from a live dune already brings semi-developed, orange-coloured soils to the surface. These, if protected from wind and water, might support vegetation similar to fully stabilized and cohesive sandy soils. It is indeed the great erodibility of all these unprotected sandy deposits that denies them a chance to accumulate a colloid fraction and to mature. The limonitic coatings of the red sand grains wash off easily, even by shaking with cold water. This explains why the sandy soils, if exposed to wind and rain, are so liable to be remobilized and to give rise to inland dunes such as found near Qadima, in the centre of Israel's coastal plain.

As a consequence of the increased building activity in Israel's coastal plain, many soil profiles have become exposed. Very often the basic arrangement shown in Fig. 1 is observed, with the red sandy soils overlaid by laminated sandstones. The clay-pan (Nazzaz) at the bottom is not always found, loose white sand often being present instead. This is consistent with the fact that raw material for the formation of clay layers is not everywhere available. Clay deposits are mostly formed, as is seen in the case of live dunes, when the wind has opportunity to erode pre-existing soils in between and underneath the moving dunes.

The boundaries of the clay layers are less sharp than the boundaries of other strata. Sand-filled crevices that cut through the clay prove that this blending is due to the expansion of the layer during the wet season and its subsequent shrinkage afterwards when it dried out. Thus a general diffusion of clay into the sandy layers bordering on it is brought about, forming an additional source for the enrichment of colloids in the sand. The richer the sand deposit becomes in colloids, the quicker the formation of additional colloidal products of hydrolysis proceeds because of the enhanced mobility of the solutions in the capillaries. In mature red sandy soil the hydrated sesquioxides are seen to become concentrated near the surface because of their predominantly ascending transport. (As a transporting medium the ascending water is more efficient than percolating rain because of its high content of protective colloids—such as colloidal silica—and its stability.)

The original strata are, of course, often covered by secondary formations. These are mostly accumulations of water-eroded material derived from the original layers of the kind described. They are furthermore sometimes mixed with grey and dark soil elements derived from the Kurkar soils found on the same or on neighbouring slopes. (Kurkar soils are the product of regular surface weathering of the cemented calcareous sandstones. Once dislocated, however, Kurkar soils probably become converted into red sandy soils, too.)

Many soil layers found overlaid by other strata are fossil soils that have become covered *subsequently* by accumulating sand or soil material and not *simultaneously* as in the cases discussed so far. Calcareous concretions occurring in them in the form of plant roots prove the former existence of a vegetative cover. In many cases, however, such concretions found in red sandy soils are only remnants of plants that became buried within the dune sand when it encroached and finally covered the wind holes already mentioned that are dug by the wind behind the slip-slopes until they reach down almost to the water-table, and then shelter a sparse vegetation.

Summary

An attempt is made to explain the formation of red sandy soils in Israel. It is suggested that the same processes may form similar soils in other coastal areas.

Where the parent material of soils consists of loose sediments, which are continually being added to, stratification of the resulting layers is mostly the result of mechanical sorting processes taking place during the deposition of material. Under Mediterranean climatic conditions, where the rate of soil formation is often comparable with the accumulation rate of material, these two processes are liable to overlap. The mechanism of the sorting processes has, therefore, to be considered when dealing with the genesis of sandy soils and associated layers.

Simultaneous deposition of different layers by aeolian sand, in Israel's coastal dune belt, is described. The sorting processes here assume a cyclic character due to the regular spacing of slip-slopes in the dune areas. While the wind tends to grade the sand towards a definite composition, the effect of this grading is periodically reversed by the opposed sorting taking place when the sand slides down the wind-shaded slip-slopes. Thus two different kinds of deposits are laid down simultaneously, one on the wind-swept slopes and one underneath the slip-slopes. While the former are gradually converted into calcareous, laminated sandstones, weathering subsequently into grey calcareous sands, the latter deposits are loose and form a layer underneath the laminated, hard ones. They thus remain protected against re-erosion, which would soon convert them into mobile sand. As these deposits retain moisture throughout the year, the finely divided iron-ore minerals, concentrated in the lower layers by mechanical selection processes, become hydrolysed and transform the sand into a red sandy soil.

Impervious clay layers are also laid down frequently underneath the

surface as the dunes shift, and have caused agricultural problems because of their pan-like character.

By accumulation of rain-eroded material from all these layers, secondary formations may result, which develop in most cases to soils that resemble very closely the wind-laid red sandy soils.

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EXPERIMENTS ON THE MECHANISM OF GLEY FORMATION

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EXPERIMENTS on the gleying of soil by fermenting sugar were described in a previous paper (Bloomfield, 1950). In an attempt to simulate the natural process more closely the possibility of using various forms of plant debris in place of sugar has been investigated.

Experimental

The following materials were tested:

1. Raw humus from Caesar's Camp, Bagshot; a light brown material, under conifers, in which plant remains were visible.
2. Peat from Furze Hill, Bagshot; a black, structureless acid material; under rushes.
3. Autumn leaves, partly withered.
4. Autumn leaves, unwithered.
5. Grass.

The peat and raw humus were ground in a Raymond mill before use, while the other materials were minced in a domestic mincing machine. The reaction mixture in each case was as follows:

Plant material	20 g.
Ammonium chloride	0·4 g.
Water	400 c.c.
Clay	*c.* 10 g.

The clay (London Clay from Bradwell Waterside, Essex) was dispersed in distilled water before being added to the reaction mixture. Each material was tested in the presence and absence of calcium carbonate.

The fermentations were carried out in 500-c.c. flasks which were swept out with nitrogen at the beginning of the experiment; samples for analysis were expelled through siphon tubes by a stream of nitrogen. The concentration of dissolved iron, determined as described previously, was used as a measure of the rate of gleying. The results obtained in these experiments are given in Tables 1 and 2 and Fig. 1.

The amounts of iron dissolved in the peat and humus experiments were small and of the same order as those reported by Gruner on the basis of essentially similar experiments (1922). However, the difficulty of obtaining clear centrifugates from the suspensions makes it probable that at least part of the iron came from suspended particles of peat; this is probably the explanation of the erratic variations shown in Tables 1 and 2. No reaction for ferrous iron was obtained with the raw humus and peat solutions on testing with $\alpha\alpha'$-dipyridyl.

Gruner found that solutions produced by treating ferruginous minerals with peat extracts gave reactions for ferrous iron when treated with ferricyanide, but it does not seem that this evidence can be taken as conclusive proof that reduction of ferric iron had taken place. In the

presence of the comparatively large amounts of organic matter present in Gruner's extracts the ferricyanide would be liable to suffer reduction to ferrocyanide and this, with ferric iron, would give Prussian Blue.

TABLE 1

Rate of Gleying. Raw Humus

Time (*days*)	$CaCO_3$ *present*	$CaCO_3$ *absent*
	Mg. Fe^{2+}/l.	*Mg.* Fe^{2+}/l.
0	7·3	11·0
1	5·6	8·0
2	6·0	6·0
4	5·4	6·0
6	3·7	4·6
9	1·4	1·6
20	1·4	6·0
46	0·5	0·2

TABLE 2

Rate of Gleying. Peat

Time (*days*)	$CaCO_3$ *present*	$CaCO_3$ *absent*
	Mg. Fe^{2+}/l.	*Mg.* Fe^{2+}/l.
0	1·3	1·5
1	0·7	0·5
4	0·6	0·9
6	0·9	0·4
8	1·2	0·2
11	0·4	0·9
15	0·8	0·8
20	0·5	0·6

While the peat and raw humus were essentially inactive, it can be seen from Fig. 1 that the other materials gave gleying effects which were comparable in speed and extent with those obtained in the sugar fermentations reported in the previous paper. (Since the addition of calcium carbonate had little effect on the reaction, these results are not shown.)

In order to determine whether the microflora of the gleyed soil material played an essential part in the process, a sample of dried grass was fermented in the presence of a suspension of London Clay which had been sterilized by autoclaving. The reaction mixture was of the same composition as in the preceding experiments. The vaccine cap and syringe method of sampling was reverted to, as this method appeared to decrease the possibility of reoxidation taking place. The variation of the pH was followed by measurements made on each sample immediately after its withdrawal from the flask. The results are shown in Fig. 2. Blank determinations carried out on the grass alone gave iron concentrations which were negligible in comparison with those of the test solutions —1·5 and 0·8 mg. per litre with and without $CaCO_3$ respectively.

Here again it can be seen that the speed and extent of the reaction are

comparable with those obtained in the sugar fermentations. The most significant feature, however, is that the only micro-organisms present were those introduced with the dried grass. It follows, therefore, that either the specific 'gleying bacteria' were present in the dried grass or

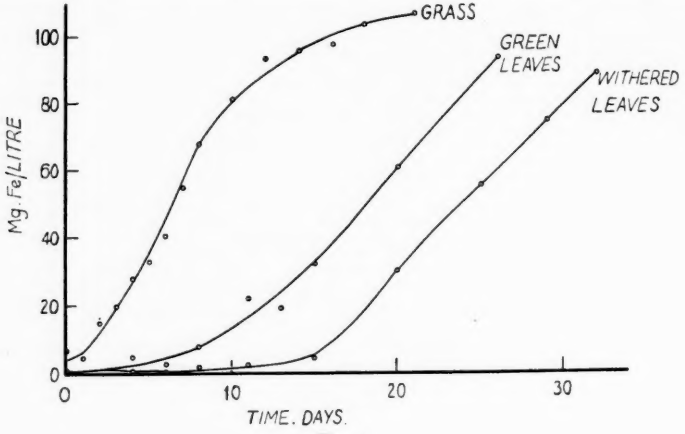

FIG. 1

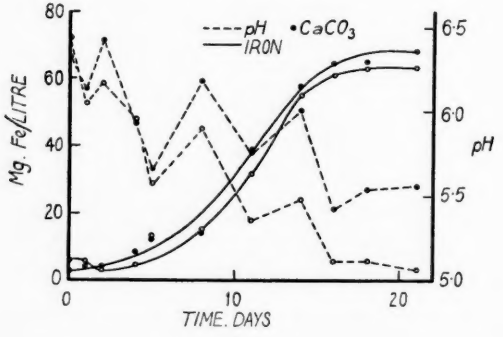

FIG. 2

that the process is a side reaction of the fermentation and not itself intrinsically a micro-biological process.

It was found that grass fermented in the absence of ferric oxide gives extracts capable of causing very rapid reduction of ferric iron in solution—a reduction too rapid to be caused by microbial action. The variation of this reducing power during the course of fermentation was investigated in order to determine the relationship existing between the reducing power of the extract and the actual production of ferrous iron in the fermentation experiments.

Ten grammes of grass were suspended in 500 c.c. of distilled water in a flask fitted with a siphon tube for sampling. The flask was swept out

with nitrogen and incubated at room temperature. Samples were expelled through the siphon tube by a stream of oxygen-free nitrogen; a measured volume of the extract was treated with a small excess of ferric chloride and the Fe^{2+} produced determined colorimetrically with dipyridyl, after removal of excess Fe^{3+} as the hydroxide. The results obtained with fresh and dried grass are shown in Fig. 3. Although this method of estimating the reducing capacity is obviously not very precise, it can be seen quite clearly that while the fresh grass quickly develops the greater reducing capacity, the dried grass extract possesses

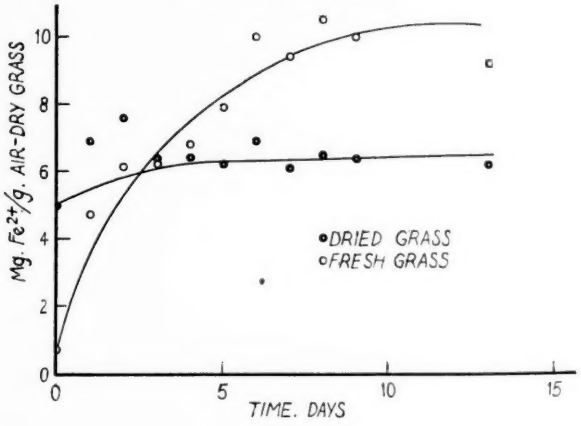

FIG. 3

an appreciable capacity for reduction of Fe^{3+} at zero time, presumably owing to fermentation of the grass during drying. It is obvious from this that there is no direct connexion between the rate of development of reducing properties in the extracts and the formation of Fe^{2+} in the gleying experiments, as can be seen by comparing Figs. 2 and 3.

On the basis of the results obtained with dried grass in the last experiment, it is possible to calculate a theoretical figure for the concentration of ferrous iron to be expected in such experiments as those illustrated in Fig. 2. Taking 6 mg. Fe^{2+} per gramme of dried grass as a conservative estimate for the reducing capacity, a value of 300 mg. Fe^{2+} per litre is obtained, i.e. a value 4–5 times the experimental figure. It follows that the extent of the reduction must be ultimately determined by some factor other than the reducing capacity of the extract; in the overall process of solution and reduction of ferric oxide, therefore, the rate-determining stage is probably the initial solution of the oxide to give soluble ferric compounds. The possibility remains, however, that a different fermentation mechanism might obtain when the plant material is fermented in the presence of ferric oxide. In order to see whether this argument may be legitimately applied to the gleying experiments, dried grass was fermented in the presence of ferruginous clay with periodic determination of the reducing capacity as well as of the ferrous iron.

The results (Fig. 4) show that while the ferrous content of the solution varied in the familiar sigmoid fashion, the reducing capacity was at all stages very much in excess of the amount of ferrous iron actually formed. It seems safe to assume, therefore, that the shape of the ferrous iron curve is determined by the rate of solution of the ferric oxide.

Having established that reduction of dissolved ferric iron may be effected non-biologically by fermentation extracts, it remained to be

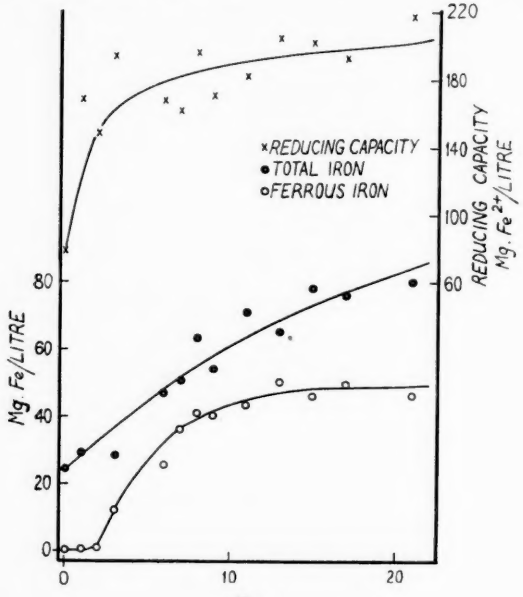

FIG. 4

seen whether the initial solution of ferric oxide involves direct microbial action. The effect of treating a sterile ferruginous clay with a sterilized extract of fermented grass was therefore investigated. The grass extract was prepared from 20 g. of dried grass suspended in 400 c.c. of distilled water and allowed to ferment anaerobically for 3–4 weeks. At the end of this time the suspension was filtered through a cotton-wool pad, the filtrate shaken with a few drops of toluene and then sterilized by filtration through a Seitz filter. A suspension of London Clay was sterilized by autoclaving and, together with the grass extract, introduced aseptically into the reaction vessel, which consisted of a separating funnel modified by the addition of a hood to the outlet. Air was removed from the apparatus by a stream of oxygen-free nitrogen, which was introduced through a glass tube carried by the bung sealing the neck of the funnel. The tube extended to the bottom of the vessel so that adequate mixing of the reaction mixture was ensured; the nitrogen escaped through a tube sealed to the apparatus below the neck of the funnel. Both tubes were plugged with cotton-wool.

The reaction mixture was adjusted to the desired pH value by addition of sodium hydroxide solution, the volume of which was derived from the titration curve for a similar grass extract–clay mixture. Samples were removed periodically for ferrous and total iron determinations, the reaction mixture being agitated by a slow stream of nitrogen during sampling. Typical results are shown in Fig. 5. The pH of the reaction mixture in each case varied by less than 0·1 unit throughout the experiment.

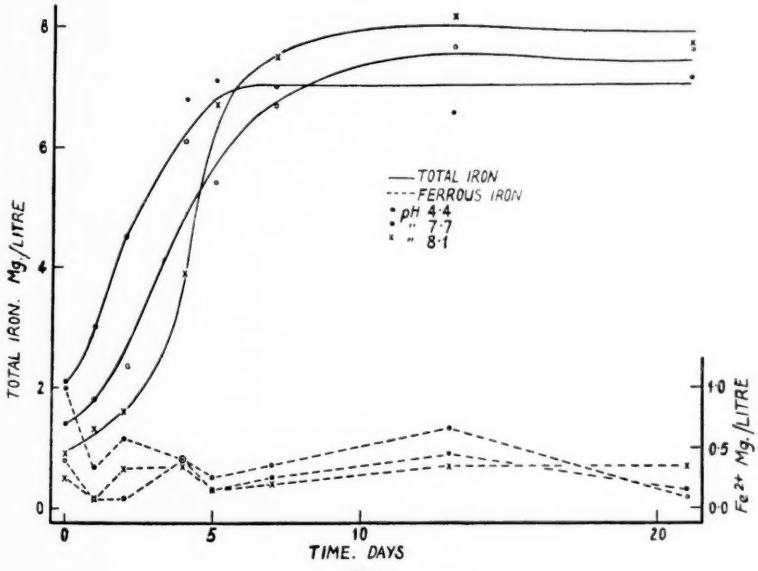

FIG. 5

It can be seen that while appreciable amounts of ferric oxide were dissolved, the ferrous iron, as determined with dipyridyl, remains more or less constant at a very low level. Tests made on the extracts with thiocyanate gave barely perceptible reactions for Fe^{3+}, and addition of a reducing agent (*p*-hydroxyphenyl glycine—photographic glycine) caused a very slight increase in the ferrous content. Despite the very low value of the ferrous iron contents, however, the capacity of the extracts to reduce Fe^{3+}, added as ferric chloride, exceeded the total iron dissolved by a factor of 5–6 throughout the whole of the experiment. This suggests that the dissolved iron is largely present either as a ferric complex which is stable to the reducing action of the grass extract or as a ferrous complex of greater stability than ferrous dipyridyl, in which case the small amount of Fe^{2+} reacting with dipyridyl would probably arise from dissociation of the 'grass' complex. The fact that the reducing capacities of the extracts decreased appreciably with time suggests that the latter supposition is correct, but it is not possible as yet to estimate the

reducing capacity with sufficient accuracy to permit a decision on this point.

In such experiments as the last, the extent of the solution of iron may vary considerably between one experiment and another; the duration of the fermentation in the preparation of the grass extract appears to be an important factor. An extract of dried grass which had been fermented for about 3 months was found to give a total dissolved iron figure of over 30 mg. per litre under the same conditions as those of the last experiment. The results, therefore, indicate that longer fermentation increases the effectiveness of the extract. Although it must be admitted that under sterile conditions the gleying effect is less marked than in the fermentation experiments, in which the soluble Fe^{2+} may exceed 100 mg. per litre, the fact remains that appreciable gleying action was produced in the sterile experiments, showing that direct microbial action is not an essential requirement for the production of gley soils.

Nature of Ferrous Solutions obtained by Grass Fermentation

The solutions obtained by fermentation of grass or tree leaves in the presence of ferric oxide are bluish-green in colour, and on exposure to air a dark olive-green precipitate is formed. Appreciable amounts of iron are retained in solution after formation of the precipitate is complete.

In order to investigate the state of combination of the iron in these solutions—whether ionic or complex—the pH of precipitation of the hydroxide was determined. The method, which has been used by Britton (1935) to characterize the stabilities of various metal-organic complexes, involves measuring the variation of the pH of the system during titration with a base. The curve connecting the volume of base with the pH shows a sharp break at the point at which precipitation commences; for equal total concentrations of the metal, the more stable the complex the higher will be the pH at which the break occurs.

Experimental

A mixture of the following composition was prepared:

Dried grass	15 g.
Ammonium chloride	0·7 g.
London Clay (*c.* 10% Fe_2O_3)	*c.* 25 g.
Water	700 c.c.

This was left to ferment anaerobically for about 4 weeks before removal of the fermentation solution for examination. Care was taken to minimize exposure to the air during the decanting and centrifuging of the solution.

The total iron content of the freshly separated solution was determined and the pH titration carried out on 50-c.c. portions. The remaining solution was treated with toluene, to inhibit continued microbial growth, and allowed to oxidize until no further precipitation took place (5 days). The filtrate was then titrated in the same manner. The filtrate gave no reaction for Fe^{3+} and the total iron content exceeded the dipyridyl

Fe^{2+} figure by a considerable amount. In view of the previous results, therefore, it was decided to use ferrous sulphate as the control in both titrations. The control solutions were adjusted to the same iron contents as the respective grass solutions.

The titration vessel consisted of a long-necked conical flask into which was fused a platinum electrode. Two side arms permitted the introduction of a KCl-agar bridge and a Beckman glass electrode. The

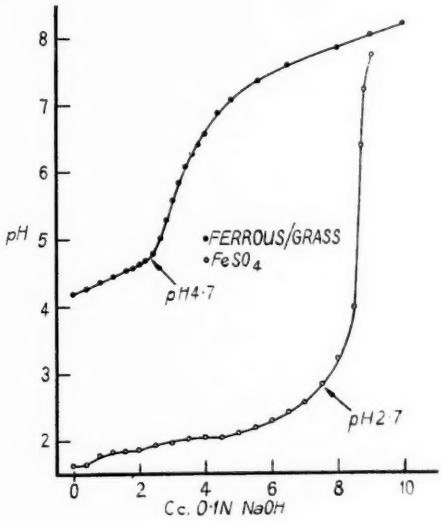

FIG. 6

apparatus was swept out with nitrogen, introduced through a third tube sealed through the side of the flask. The nitrogen escaped through the neck of the flask, which was wide enough to provide a small clearance when the burette tip was introduced. Traces of oxygen were removed from the nitrogen by passing it over heated copper and through alkaline pyrogallol solution.

Fig. 6 shows the results obtained using the unoxidized solution, containing 102 mg. Fe^{2+} per litre, compared with those obtained with a solution of ferrous sulphate of the same concentration. Owing to the ease with which ferrous hydroxide is oxidized, and to the difficulty of preparing completely oxygen-free nitrogen, the precipitated material was oxidized to some extent, despite the precautions taken to exclude oxygen. This was especially obvious in the case of the control experiments so that these results cannot be regarded as having more than comparative significance. However, the marked difference between the pH at which precipitation commenced from the grass solution and from the control (4·7 and 2·7 respectively) is sufficiently great to demonstrate the existence of a ferrous complex. Additional evidence for this is

provided by the fact that after the pH of the grass solution had reached a value of 8·2, the dark brown solution obtained after removal of the precipitated material contained 23 mg. of iron per litre, i.e. about $\frac{1}{5}$ of the initial concentration.

The results obtained with the oxidized solution are illustrated in Fig. 7, from which it can be seen that the breaks in the curves were

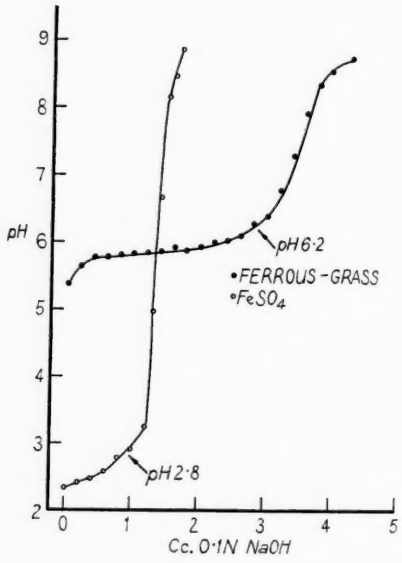

FIG. 7

formed at pH 2·8 and 6·2 for the control and test solutions respectively. In this case, however, no visible precipitate was formed in the grass solution, although a final pH of 9 was recorded. The solution at this stage was quite clear and had a dark red-brown colour: qualitative tests made with thiocyanate and dipyridyl did not suggest that any oxidation had taken place. The solution remained clear after standing overnight in an open beaker, although qualitative tests suggested that slight oxidation had occurred.

From the foregoing experiments it appears that the iron in the fermented grass solution was in part present as a very stable ferrous complex, while the remainder, the greater part, was present in a considerably less stable complex form. From the close agreement between the iron contents of the alkaline unoxidized filtrate and the filtrate from the oxidized solution (23 and 20 mg. per litre respectively) it is reasonable to assume that it is iron in the same state of combination which suffered precipitation from the original solution when this was subjected either to oxidation or to an increase in pH.

Fixation of Ferrous Iron by Ferric Oxide

The work described in this section originated in an attempt to develop a method for the estimation of ferrous iron in gley soils.

Morrison and Doyne (1914) investigated the use of dilute acids as extractants in this connexion and found that, in the presence of soil organic matter, such treatment caused extensive reduction of ferric iron.

Ignatieff (1937–41) found that this difficulty could be avoided by using 2 per cent. aluminium chloride as the extractant—a rather surprising result in view of the marked hydrolysis of this compound. Unfortunately the writer has been unable to substantiate this observation with the gley soils at his disposal.

Experiments were carried out to determine whether the reduction of ferric iron could be overcome by using sufficiently mild acid conditions in the extraction.

Experimental

Air-dry London Clay was ground to a fine powder and exposed to the air for several weeks to ensure complete oxidation. A weighed amount of the clay was treated with a measured volume of ferrous sulphate solution, and after standing for about 30 minutes the mixture was centrifuged; the centrifugate was decanted off and its ferrous content determined. Knowing the amount of ferrous iron added originally the amount remaining with the clay could then be calculated. The clay–Fe^{2+} mixture was then extracted exhaustively with M-ammonium acetate solution and the ferrous content of the combined extracts determined. The recovery of Fe^{2+} obtained in this manner is shown in Table 3.

TABLE 3

Effect of pH on Recovery of Fe^{2+} *from London Clay*

(*Mg./g.*)	*pH 6*	*pH 5*	*pH 4*	*pH 3*
Fe^{2+} added . . .	1·03	1·03	1·03	1·03
Fe^{2+} in centrifugate .	0·14	0·18	0·29	0·28
Fe^{2+} left with clay .	0·89	0·85	0·74	0·75
Fe^{2+} extracted . .	0·02	0·06	0·07	0·11
Fe^{2+} 'fixed' . . .	0·87	0·79	0·67	0·64

It can be seen from these results that something in the nature of fixation of the ferrous iron had taken place. As the London Clay had not been subjected to any cleaning process, the fixation could have been caused by organic matter, ferric oxide, or, less probably, by the clay mineral itself. It was found that London Clay, from which organic matter had been removed by treatment with hydrogen peroxide, gave the same amount of fixation as the untreated clay; it is unlikely, therefore, that the organic matter was responsible for the effect.

In order to avoid possible interference by residual organic matter in the investigation of the role of the ferric oxide, samples of kaolin were prepared on to which ferric oxide was precipitated to give products containing 2, 8, and 10 per cent. ferric oxide respectively. After washing

free from dissolved salts the preparations were dried at 105°; it was found that this treatment did not render the ferric oxide sufficiently insoluble to withstand the subsequent treatment with ammonium acetate, but heating at about 180° for a short time gave a satisfactory product.

Weighed amounts of these clays were then treated with ferrous sulphate and extracted with ammonium acetate at pH 5 as before. The results are given in Table 4.

TABLE 4

Fixation of Fe^{2+} *on* Fe_2O_3*/kaolin*

% Fe_2O_3 *on clay*	*Mg.* Fe^{2+} *fixed per g.* Fe_2O_3
0	nil
2	10
8	12
10	8

It is apparent from these figures that the ferric oxide is responsible for the fixation. Ferric oxide alone was found to behave in a similar way.

It was shown in a similar manner that ferric oxide is capable of fixing ferrous iron in the complex form produced in the grass fermentation process:

Fe^{2+} added 29·0 mg. per gramme Fe_2O_3
Fe^{2+} fixed 8·0 „ „ „ „

In this case the ferric oxide acquired a dull brown colour immediately the ferrous-grass extract was added, suggesting that under these conditions organic matter is taken up in addition to ferrous iron.

The fixing capacities of synthetic α-, β-, and γ-ferric oxides were compared, using ferrous sulphate. It was found that, weight for weight, the hydrated α-form (Göthite) had by far the greatest capacity; however, X-ray diffraction patterns of the three forms showed that the α-material consisted of very much smaller particles than the others; it is not known as yet to what extent the greater capacity of the Göthite is a function of the consequent greater surface area.

It was noticeable that the artificial Göthite contained many comparatively large aggregates and, no doubt because of this, duplication of results was not very good. This difficulty was overcome by precipitating the ferric oxide in a suspension of kaolin. Weight for weight of ferric oxide, the kaolin–Fe_2O_3 preparation, which has been used exclusively in subsequent work, had a much greater activity than the pure oxide, presumably again because of differences in the surface areas.

Fig. 8 shows the variation of fixation with time.

By using a comparatively high concentration of ferrous sulphate it was possible to increase the extent of the fixation to a degree which made feasible an investigation of the valency state of the fixed iron.

Ferric oxide-kaolin (10 per cent. Fe_2O_3) was treated with ferrous sulphate solution for 2 hours and then centrifuged and washed. Determination of the Fe^{2+} content of the combined centrifugate and washings

gave the extent of the fixation. The ferrous iron remaining in association with the ferric oxide was determined by dissolving the residue in hydrochloric acid and titrating potentiometrically with 0·02 N-cerate solution. The results, given in Table 5, show that recovery of Fe^{2+} from the ferric oxide was negligible in comparison with the amount abstracted from the solution. Determination of the total iron remaining

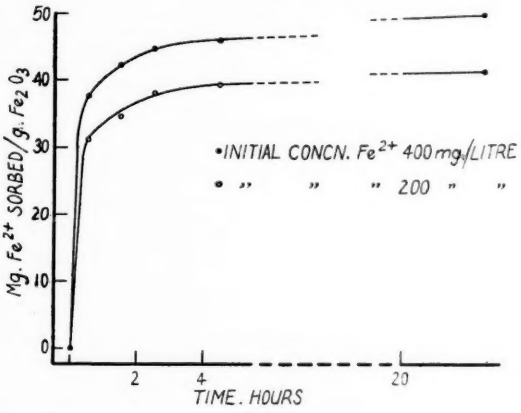

FIG. 8

in solution showed this to be no greater than the figure for the ferrous iron, and since neither the ferrous sulphate alone, nor the ferrous sulphate–kaolin mixture, was appreciably oxidized under the same conditions, it can only be assumed that the 'fixed' ferrous iron had been oxidized on the surface of the ferric oxide.

TABLE 5

Oxidation of Fe^{2+} *on* Fe_2O_3

194 mg. Fe^{2+}/g. Fe_2O_3. 2 hours

	Kaolin		*Kaolin*–Fe_2O_3	
Mg. Fe^{2+} removed from solution	13	11	48	39
Mg. Fe^{2+} removed from clay .	8	7	4	5
Mg. Fe^{2+} oxidized . . .	5	4	44	34

Equivalent oxidation on $FeSO_4$ blank, 2 mg.

In these experiments, because of the relatively slow rate of oxidation of ferrous sulphate solutions, no attempts were made to exclude atmospheric oxygen during the treatment of the ferric oxide; it therefore remained to investigate the effect of excluding oxygen during the process. The apparatus used for this purpose is illustrated in Fig. 9. Flask *A* contained distilled water which was boiled to expel oxygen and cooled to room temperature in a current of oxygen-free nitrogen. The reaction vessel *B* was dried and an accurately weighed sample of ferrous sulphate introduced into the graduated bulb *C*. Next, by means of a

bent funnel, a known amount of ferric oxide–kaolin mixture was introduced into the tubule *D*. The two parts were then assembled and the reaction vessel swept out with nitrogen introduced through the by-pass tap *E*. *B* was then filled to the graduation with water forced over from *A* by the nitrogen stream. After bubbling nitrogen through the solution for a short time to ensure adequate mixing, the taps were closed and the ferric oxide mixture shaken into the solution. The mixture was agitated

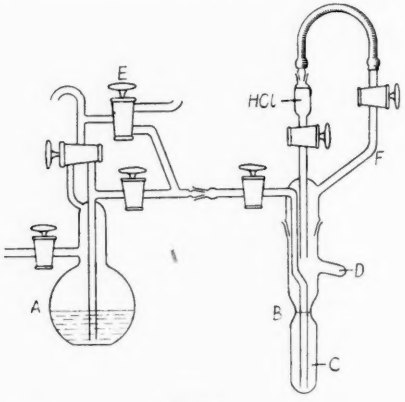

FIG. 9

occasionally by a stream of nitrogen over a period of 3 hours, at the end of which period tube *F* was swept out with nitrogen and connected to the neck of the dropping funnel. The reaction was then stopped by running in the acid from the dropping funnel. Once solution of the ferric oxide was complete the mixture was washed into a beaker and the Fe^{2+} determined by cerate titration as before. Similar determinations were made in beakers left open to the atmosphere as controls. It can be seen from Table 6 that ferrous sulphate alone suffered slight oxidation when exposed to the air, while in the presence of ferric oxide, oxidation was quite marked. In the absence of air the presence of ferric oxide had no effect.

A possible mechanism for the fixation suggested by these results is that initially ferrous iron is adsorbed on the surface of the ferric oxide and is thereby rendered sufficiently readily oxidizable for this to be rapidly effected by dissolved oxygen present in the system.

TABLE 6

Effect of Air on Oxidation of Fe^{2+}/Fe_2O_3

Mg. Fe^{2+} oxidized per g. Fe_2O_3

$FeSO_4$/*air*	$FeSO_4/Fe_2O_3$–*kaolin*/N_2	$FeSO_4/Fe_2O_3$–*kaolin*/*air*
0·55	0·27	15·2
	0·22	17·4
	0·25	14·3

The degree of fixation obtained in successive equivalent treatments of α–FeOOH–kaolin with ferrous sulphate solution is shown in Table 7.

TABLE 7

Successive Fixation of Fe^{2+} *by* Fe_2O_3

	Mg. Fe^{2+} *fixed per g.* Fe_2O_3
First treatment	18·5
Second ,,	5·0
Third ,,	3·3

A possibility suggested by these results is that the formation of the B horizon of a podzol might be due to some such mechanism. It can be seen that as the newly acquired ferric oxide is capable of fixing further amounts of ferrous iron, a self-regenerating cycle may be postulated to account for the continued precipitation of ferric oxide which is involved in the formation of a B horizon or an iron pan.

Discussion

If it is assumed that the reduction of ferric iron in gley soils is caused solely by specific micro-organisms, it is necessary to assume a very widespread distribution of the particular organisms in order to explain the world-wide distribution of this soil formation. On the other hand, if the reduction may be caused by the normal degradation products of plant debris, both the widespread distribution and the range of pH values of these soils is readily explained.

A theory for the mechanism of gleying must be capable of accounting for the numerous instances in which the pH value of the soil is near neutrality. Hence the development of high acidities in the fermentation experiments precludes the drawing of close analogies between the laboratory and field processes. The experiments on the sterile grass-extract ferric-oxide system, however, show that under these conditions no significant change in pH takes place during the process. This suggests that the sterile experiment represents a much closer approximation to the natural process. The view put forward here, that the production of gley soils is caused, at least in part, by plant degradation products, therefore seems to provide a more satisfactory explanation than does that involving the sole agency of specific micro-organisms. The statement of Zavalishin (1928) that the water-soluble organic matter is higher in the G than in the A horizon assumes considerable significance in this connexion.

The production of soluble ferrous compounds is the characteristic feature of the artificial gleying process, yet Zavalishin found that the chemical composition of a gleyed soil did not differ essentially from that of corresponding ungleyed material. If, as seems probable, the materials used were obtained from completely waterlogged sites where removal of

soluble products would be virtually negligible, this is not perhaps surprising. On the other hand, examples are well known in which marked changes in chemical composition have been caused by gleying. As an example one may quote those cases in which the soil contains iron stains or concretions. In such soils the iron content of the whole soil does not differ significantly from that of corresponding ungleyed material, although it is apparent that appreciable local changes in composition have been produced. Another example is provided by those intermittently waterlogged soils in which only the surfaces of the structural elements are bleached (Robinson, 1949). This type is well illustrated by the Rothamsted subsoil. The profiles of such soils are characterized by the presence of pronounced fissures through which preferential drainage occurs. Thus the plant decomposition products, which are responsible for the solution and reduction, penetrate the soil mass by diffusion from the surfaces of the structural elements. Clearly the reaction will commence at these surfaces, and part of the reaction products will diffuse into the elements. If the Rothamsted subsoil is examined in detail, it is seen that the bleached surfaces are underlaid by thin iron enrichment zones which must be formed by the redeposition of the iron removed from the gleyed layer, presumably by virtue of the fixation process. Iron determinations on the Rothamsted material gave the following results, calculated as Fe_2O_3:

Bleached zone	3·4%
Enriched zone	10·1%
Bulk sample	9·3%

There is thus no question that in such cases gleying results in pronounced translocation of iron.

In view of the foregoing experiments it seems inevitable that the water-soluble products of plant decomposition, extracted from the surface soil, would cause solution and reduction of ferric oxide encountered during their passage down the profile. Presumably, once the capacity of the extract to dissolve more iron has been exhausted, the ferrous iron would be immobilized to some extent by sorption on ferric oxide in the lower layers. The experiments on the fixation of ferrous iron indicate that subsequent reoxidation of the sorbed ferrous iron would occur comparatively readily once the conditions became slightly aerobic—such conditions as would probably arise during dry weather, for example. Once reoxidized, the ferrous iron would provide a fresh medium for further fixation, and the process would thus be regenerative.

The fixation and oxidation of ferrous iron on ferric oxide appears to resemble the phenomenon described by Selwood (1948, 1949), to which he has given the name 'valence induction'.

Acknowledgement

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A CYLINDRICAL GYPSUM BLOCK FOR MOISTURE STUDIES IN DEEP SOILS

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Introduction

SOIL fertility studies under Arabica coffee described elsewhere have shown that, for interpretation of fertilizer problems, a continuous record of the availability of water is needed throughout the 15-ft. root-range of the trees. This paper describes the development and quantitative testing of a cylindrical screened electrode gypsum unit which can be conveniently placed by soil auger to such depths. Details are given of simple robust hand-driven dynamo-ohm-meter instruments suitable for the use of native assistants under tropical conditions.

Soil Profile Characteristics

These coffee soils are described by Gethin Jones (1948) as the Kikuyu Red Loam series. They have been developed *in situ* by past ages of intensive leaching of deep beds of lava and tuff. A high pore-space has permitted free root penetration to depths of over 20 ft., and the subsoil remains permeated by root tunnels of the past climax vegetation, which was, over most of the area, heavy forest. Additional very numerous channels have resulted from termite action. Thus although these soils are characteristically free draining, the movement of water takes place mainly down the major channels. This has been confirmed by the author by percolation measurements made on undisturbed soil cores, and also by observations made from the walls of freshly dug pits. Soil moisture studies under field crops must therefore be conducted in a profile as little disturbed as possible.

Placement of Soil Moisture-measuring Units

The principle of the gypsum-block technique of Bouyoucos and Mick (1940, 1947) is most promising for studies of this type, but, for the reasons described above, a first consideration had to be an improvement in the method of placement. Bouyoucos and Mick describe the preparation of a hole by a 4-in. post-hole auger, in which their flat rectangular gypsum units are placed in vertical array, the soil being packed around them in the correct order. Each gypsum block is thus surrounded by a considerable volume of disturbed soil. This method is not appropriate to the coffee soils described above. Rayner (1946) found considerable difficulty in placing rectangular blocks to the depth of coffee roots, but obtained encouraging preliminary results with them. Cylindrical units, 1 in. in diameter and 3 in. long, were therefore designed (Pereira, 1947) and are described below.

These have proved very convenient for field installation. Vertical holes are drilled by a 1½-in. diameter soil auger to within 3 in. of the block position, the soil being set aside in the correct order for refilling. The

final 3 in. are carefully drilled with a sharp 1-in. bit, to form a socket into which the wetted block slips snugly. The block is held in a rubber socket, fashioned from a laboratory bung, which is screwed to the end of a wooden rod (Fig. 1). The block leads are carried through the slot in the rubber and along a groove in the wooden rod. A slight tension is maintained in the leads during placement, and the resistance of the block is checked before the hole is refilled. The rod carries a depth scale by which the final position of the block is confirmed. The soil is rammed back firmly, to avoid drainage, but puddling must be avoided in soils

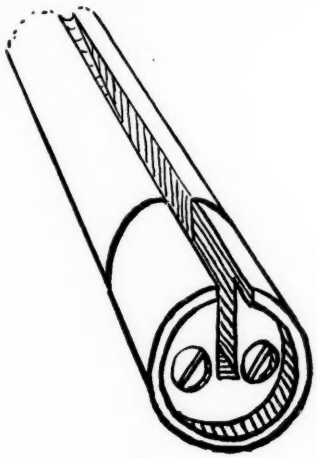


FIG. 1

with high clay content since the subsequent shrinkage on drying has been observed to form an annular space down which roots may penetrate. The gypsum cylinder is thus left surrounded by a mass of undisturbed soil, into which the inactive volume of the well-packed auger-hole makes a minimum intrusion.

Design of Screened-electrode Unit

The cylindrical block can be constructed either with straight-wire electrodes, as used by Bouyoucos and Mick, or with a cylindrical grid outer electrode as proposed by Slater (1942). The latter used an outer cylindrical electrode closed at one end. This is not so easy to prepare as is the flat block and does not appear to have been put into general use. The advantage of the concentric over the straight-wire electrodes is that all of the metering current is retained within the standardized conditions of the gypsum electrolyte. With the flat block a substantial proportion of the metering current passes outside the block when the soil is wet. Slater and Bryant (1946) reported that cylindrical blocks had a longer life in soil, but that they found no improvement in performance over the Bouyoucos and Mick design. Standardized current conditions are

required for the use of the measuring instruments described below, and the cylindrical metal case gives useful mechanical strength to units for deep placement in hard subsoils. Concentric electrodes were therefore employed. A design of unit readily constructed in a laboratory without workshop facilities is shown in Fig. 2. The leads are of flat plastic-covered twin lamp-cord. The central electrode is fashioned by solder-coating one lead and then reinsulating the extremity by slipping on plastic tubing, to form an anchor-loop in the gypsum. Two precast gypsum disks, accurately drilled to take the centre electrode, act as

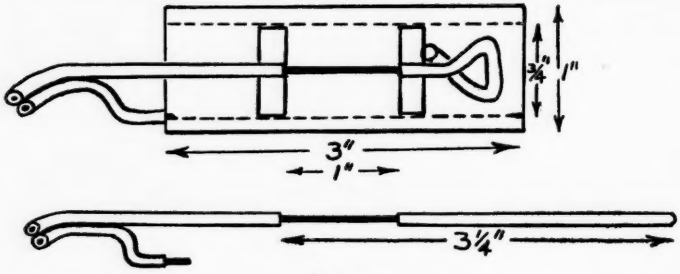


FIG. 2

spacing pieces for the cylindrical grid which forms the outer electrode. Monel metal was not available, and the cylinders were therefore made from solder-coated brass mosquito-gauze. In soldering the second lead to the outer cage, sufficient slack is left to ensure that any mechanical strain incidental to deep placement is taken by the well-anchored central lead.

The cage is clamped into a mould cut from plastic tubing, which is split longitudinally and secured by split-rings cut from the same tubing. A carefully standardized mix of dental-quality gypsum is poured in, with vigorous tapping to free entrapped air. On removal from the mould, the blocks are gently immersed in distilled water and left to cure, in a temperature maintained steady within $\pm 1^{\circ}$C. Resistance is measured daily, and the blocks are considered to be 'cured' when the saturated resistance has become steady, which takes from 2 to 7 days. Failure to cure blocks invariably leads to subsequent fluctuations in their saturated resistance. These hand-made blocks required individual calibration. Uniformity sufficient for the calibration of a few blocks only from each batch could not be attained in the laboratory.

After 3 years of testing in field and laboratory, this design was submitted to the research division of Messrs. Baird and Tatlock (London) Ltd., with the object of securing a more uniform manufactured product. Matthews (1951) has described the modifications adapted for manufacture. These were the substitution of monel-metal gauze for the solder-coated brass, the use of perspex instead of gypsum for spacers, and the fashioning of a separate cylindrical central electrode. The centre lead passes through this cylinder for secure anchorage. The blocks are manufactured in both 1-in. and $\frac{5}{8}$-in. diameters, and are extremely convenient for use in very deep subsoils (Fig. 3). The saturated resistance of batches of fifty blocks lie within 5 per cent. of the mean (of about 40 ohms).

Field Instruments for Measurement of Resistance

Portable electronic instruments for the production and measurement of the necessary alternating current have proved difficult to operate under East African conditions. Difficulties have arisen both through failures of instruments themselves and through the limited standard of training of many of the native field assistants available. Rayner (1946) used an oscillator-rectifier milliameter circuit similar to that described by Colman and Hendrix (1949), while the author has used an oscillator and bridge similar in principle to that described by Bouyoucos and Mick (1947). Neither type of instrument proved satisfactory under the local conditions. Better success has been obtained by using a modification of a well-known insulation-testing meter, the essential features of which are a robust hand-operated dynamo producing alternating current and a direct-reading resistance meter. Agreement with the more accurate capacity-balanced Wheatstone's bridge was sufficient for practical field use, and an improved design has now been developed for this work by the B.T.L. Research Division (Fig. 4). This instrument has a scale calibrated directly to log-resistance, with a range-switch which alters the log index. This gives the necessary sensitivity throughout the range from 10 ohms to 10 meg. ohms, and employs much lower voltages than those used by insulation meters. All such instruments record the impedance rather than the true resistance of the gypsum blocks, and the readings deviate from those of the capacity-balanced bridge at low values. Provided that the calibration and field work are done with the same type of instrument, this offers no difficulties. By means of a conversion scale, bridge and resistance-meter readings can be interchanged, when necessary, for concentric-electrode blocks, but it has not been found possible to obtain reproducible conversion curves with the flat pattern for wet soils.

Calibration of the Gypsum Units

The rapid and convenient open-pan method described by Bouyoucos and Mick (1948) has given erratic results with these lateric subsoils, especially at the wet end of the scale. This appeared to be caused by failure of the water to move freely enough through these soils to maintain an effective uniformity of moisture content in a sample of soil dried on the bench in a small open pan. Results were somewhat improved by slower drying in humidity chambers, but agreement in successive drying cycles was poor. Wire-gauze cages, as described by Kelly (1944), gave rather better results provided that the blocks were surrounded by a uniform thickness of soil. Their cylindrical shape facilitated this. Temperature control appeared to be critical, and neither cages nor open pans gave sufficiently reliable results with this soil type. The critical studies of the drying of thin layers of disturbed soil, carried out by Keen, Crowther, and Coutts (1926), emphasize the inherent difficulties of such methods.

Compressed-air membranes as described by Richards (1941) appear to offer a useful method, but attempts to obtain diaphragms of adequate

strength and durability have not yet succeeded. For low tensions, asbestos tension tables as described by Jamison and Reed (1949) have given no changes in resistance with soil samples containing blocks.

Anderson and Edlefsen (1942) showed the advantages of live roots for

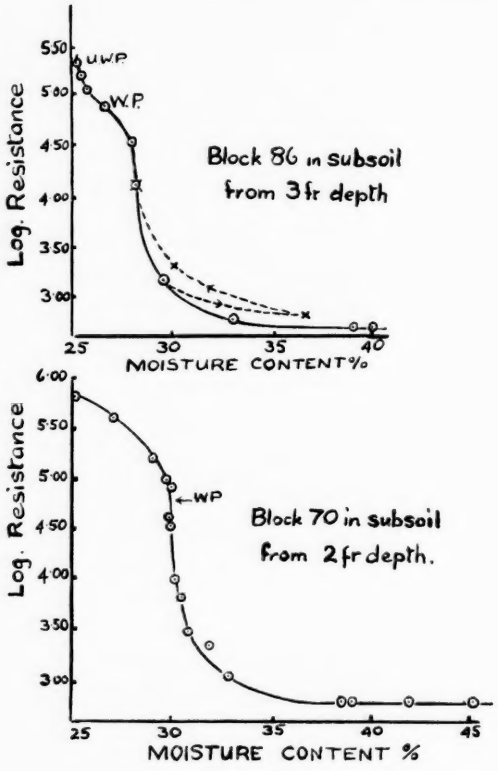


FIG. 5 *a*, *b*

calibration of blocks. Since a study of the wilting-points in these deep subsoils was necessary, the blocks were included in soil samples set up for wilting-point determinations. The procedure followed for sieved soils was that of Furr and Reeve (1945), the plants being taken in most cases to their ultimate wilting-points. Undisturbed cores were also used, but difficulty was encountered in obtaining a satisfactory growth of sunflower roots in some compact samples of deep subsoils. The method proved extremely tedious; resistance-weight curves were first obtained for the blocks, and estimates of the weights of sunflower seedlings were obtained from stem-length and leaf-area measurements with sufficient accuracy for this purpose. From daily observations of assembly weight, block resistance, and sunflower dimensions it was found possible to

obtain reproducible calibration curves, with direct observations of block resistance at the first permanent and at the ultimate wilting-points.

The behaviour of the gypsum blocks during the wilting and recovery of the sunflower seedlings was interesting. The onset of wilting was

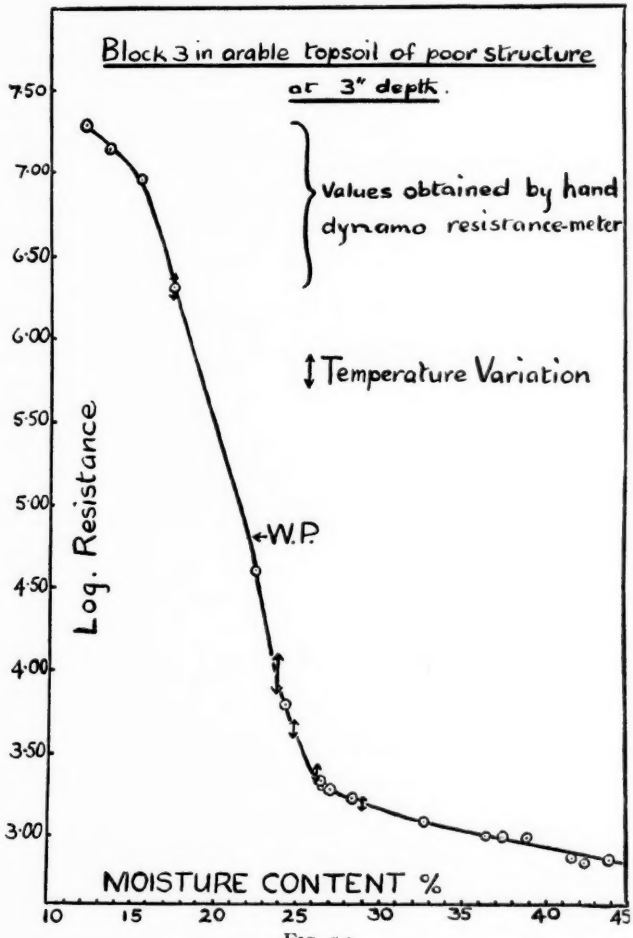


FIG. 5*c*

always accompanied by a sharp drop in resistance. The plants were then placed in the dark for recovery, in bell jars over open water, the interiors of the jars being generously sprayed to ensure saturation of the contained air. As turgor was recovered block resistance rose, often to exceed that reached before wilting. Thus although transpiration was

presumably negligible, the recovery of turgor by the plant was accompanied by re-establishment of increased tension throughout the soil mass.

Unless each cycle began at saturation, hysteresis effects intervened. It was therefore not possible to rewet a sunflower assembly to field capacity by the addition of the calculated quantity of water. Fig. 5 *a* illustrates the loop obtained when this was attempted. The first permanent wilting symptoms, as defined by Furr and Reeve (1945), occurred at a point where resistance was changing rapidly. The values usually obtained lay between 50,000 and 80,000 ohms, and a value of log $R = 4{\cdot}8$ was taken as an average figure for the limit of water available to plants.

The calibration curves were similar to those described in the extensive literature of this method, and are illustrated in Fig. 5 *b*. Some sigmoid and linked sigmoid curves were obtained: using the hand-dynamo instrument and sufficient repetitions of the wire-cage or open-pan methods, it was found possible to obtain reproducible curves far beyond the range of water available to plants. This is of value in quantitative estimates of the water requirements of sunbaked tropical arable soil. An example is given in Fig. 5 *c*.

When sufficient replication of profile sets of these blocks is used on a practical problem, the need to correct the large quantity of resistance data for temperature becomes onerous. By reading the blocks before 10 a.m. daily, it was found that temperature changes of importance would occur only with the uppermost blocks at a depth of 3 in. A year's daily readings of soil thermometers set near the blocks in arable soil showed that the range of temperatures at 9 a.m. was from 60° F. to 75° F. The resistance change between these temperatures at five different moisture-contents for blocks in soil from near the 3-in. depth is shown in Fig. 5 *c*. No temperature corrections of field data have therefore been made.

Quantitative Interpretation of Gypsum Block Records

Bouyoucos and Mick (1940, 1947) showed that flat gypsum resistance blocks give an excellent qualitative record of soil moisture changes, with approximate quantitative interpretation. Haise and Kelly (1946) calibrated these blocks on the pressure-membrane apparatus of Richards and Fireman (1943) to soil moisture tension. Kelly *et al.* (1946) showed that uncalibrated resistance records gave a very effective method of controlling irrigation, and large-scale commercial application was described by White (1946). Bouyoucos (1950) has reported striking improvements in the efficiency of irrigation when controlled by gypsum blocks. For these, and for many research purposes, detailed quantitative calibration is unnecessary, but for studies of the accumulation of moisture reserves within the root-range of crops during monsoon rains, and their rate of exhaustion during drought, a technique recording inches of water per foot of soil is required. Soil records can then be directly compared with rainfall, evaporation, and hydrological estimates.

For these purposes all absorption block techniques are handicapped by those hysteresis effects between tension and moisture content which

are well established as implicit properties of porous media (Haines, 1930). The tension equilibrium between a porous block and surrounding soil is thus reached at a soil moisture content which depends on the manner of wetting or drying. All quantitative interpretation must depend upon the consistent relationship between tension and soil moisture content found in continuous drying curves which start from saturation. Such conditions can be assured during calibration of blocks and soils in the laboratory, but in the field, even under a monsoon-type

TABLE I

Percentage Moisture-content on Dry Weight of Soil

Oven drying of samples			*Block records*	
Bare fallow	*Ranges*	*Means*	*Ranges*	*Means*
Conditions: Very dry before 'rains'				
Depth				
3 in.	16·6 to 17·7	17·2	18·0 to 21·5	20·0
6 in.	20·1 to 22·5	21·0	18·0 to 25·4	21·3
1 ft.	27·7 to 32·1	29·8	26·2 to 29·5	27·7
2 ft.	33·4 to 34·5	33·6	33·0 to 36·8	34·6
Standard error of means		±0·84		±1·35
Conditions: Two weeks' drying, after end of 'rains'				
Depth				
3 in.	23·3 to 26·1	24·7	25·5 to 30·0	27·5
6 in.	28·2 to 30·9	29·7	31·0 to 32·5	31·8
1 ft.	30·2 to 32·8	31·5	31·7 to 37·0	35·2
2 ft.	31·3 to 34·3	32·6	34·5 to 37·0	35·9
Standard error of means		±0·81		±1·26

distribution of rainfall, there are frequent interruptions of continuous drying. Richards and Weaver (1943) measured hysteresis effects on a range of soil types. Although broad loops were traced by some soils, they did not consider that these would be found under field conditions, in which complete saturation is rare. They suggested that the effect could be minimized, in their ceramic weighed sorption blocks, by matching block porosity to soil types. No successful attempt to do this with gypsum blocks has been reported, and the substitution of ceramic or fabric media, in which pore-space is more readily controlled, loses the valuable buffering effect of gypsum, so that resistance is effected by small changes in salinity (Coleman and Hendrix, 1949). The quantitative performance of gypsum blocks can therefore be assessed only by direct field trial in any soil type. Such trials must include estimation of field moisture variability and are inevitably laborious. Slater and Bryant (1946) made a thorough field study of flat gypsum blocks on a sand and on a silt loam. They found agreement between gravimetric sampling and block records to be effective over a limited range, from wilting-point to 29 and 57 per cent. respectively of the capacity of each soil for available moisture.

Facilities for such a large-scale trial were not available, but six profile sets of individually calibrated blocks were compared with soil sampling to 3 ft. in bare fallow. From 30 to 90 soil samples were taken at the beginning and end of each rainy season. Attempts at a similar comparison among roots of coffee-trees were defeated by the highly variable distribution of soil moisture among the roots in wet conditions. Typical results for fallow soil are shown in Table 1.

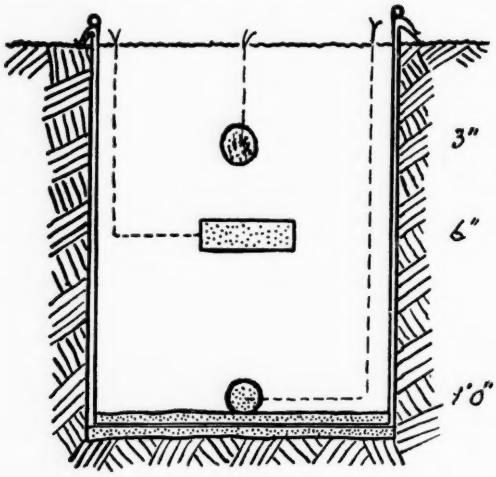


FIG. 6

A more direct assessment was obtained from a small pilot-model of a weighed soil column in which the soil is drained under subsoil tension. Observations throughout 1947 and 1948 had shown that the seasonal drying of bare weed-free fallow could affect blocks placed 2 ft., 3 ft., and 4 ft. deep, but that only those in the first foot suffered regular complete cycles of wetting and drying. The first foot was therefore studied in detail as follows.

A column of soil weighing approximately 50 lb. was isolated by digging away surrounding soil, and a metal sleeve was slipped over it, fitting it very closely. Calibrated gypsum blocks were inserted horizontally at 3 in., 6 in., and 1 ft. as the sleeve was put on. Stout wire mesh was soldered on, and around it a gypsum plate 1 in. thick was cast directly on to the soil at the base of the column. A hole was then excavated in uniform bare soil and lined with a casing into which the column would slide easily (Fig. 6). The subsoil was carefully scraped level and a gypsum plate cast into it. The object was to follow soil moisture changes by direct weighing, while avoiding the waterlogging which usually occurs, in spite of carefully prepared drainage, at the base of conventional lysimeters. Two similar sets of cylindrical gypsum blocks were placed in the soil 3 ft. on either side of the column. Tension distribution within the column could thus be compared with that of the undisturbed soil

profiles on either side. After 12 months of frequent observations, including two wet seasons and two severe droughts, the assembly was dismantled, the soil oven-dried and weighed, and the blocks recalibrated. No appreciable deterioration had occurred. Calibration had not changed over the upper range of the blocks, but all showed a small increase in saturation resistance. This effect has been observed with all blocks used in the field; it occurred with concentric and with plain wire electrodes,

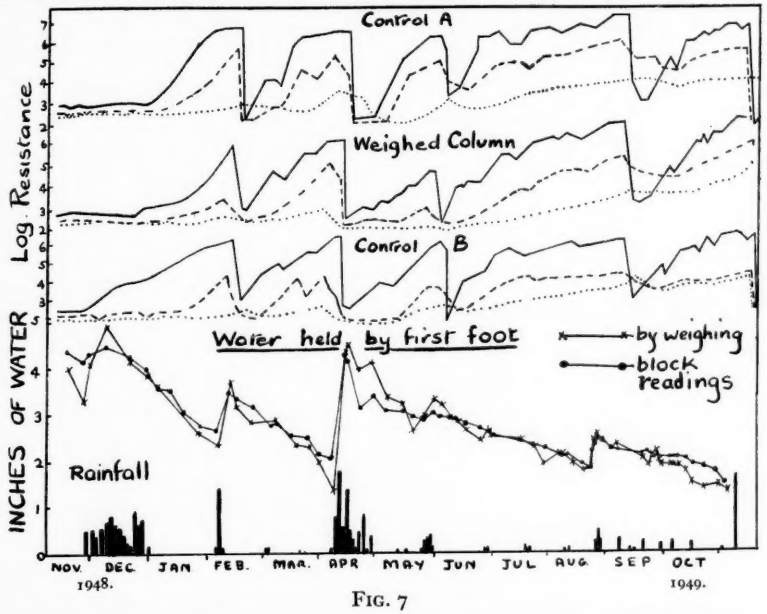


FIG. 7

and with plaster of Paris from two widely different commercial sources. The cause has not been determined.

The water content of the gypsum base was found from the resistance of the block in contact with it, and the total weight of the water in base and blocks was subtracted from each weighing. It was less than 3 per cent. of the water held by the soil. During wet periods weighings were infrequent, in order to avoid disturbance of drainage; in dry weather frequent weighings were made. Excessive drying of the base of the column eventually resulted. The results are shown in Fig. 7. While exact agreement in tension distribution was not to be expected in view of the coarse porosity of the gypsum base, the conditions were very similar throughout the year. A comparison of the soil moisture-content estimations from blocks and from direct weighing was thus carried out under fair field conditions. The agreement is fair only for the drier part of the range. It appears sufficient to permit the quantitative use of gypsum blocks in this soil type where the top foot holds 3 in. of water or less. In terms of availability to plants, this includes 56 per cent. of the 1·40 in. of water held between field capacity and wilting point. Agree-

ment should be better at greater depths, and the above results are sufficiently encouraging to justify a more extensive study of this type of soil column. The column should preferably have a ceramic base matching the subsoil porosity, and may then offer a useful method of checking the quantitative range of gypsum blocks for further soil types. The variability of subsoil density is also an important factor, and the estimation of the replication required in density determinations is an essential part of this study. These lateritic soils become extremely hard when dry, and the physical difficulties of an adequate sampling programme are greatly increased. The quantitative use of gypsum blocks to establish the limit of drying of the profile by vegetation is thus convenient. Throughout the season they give a reliable estimate of the duration of available moisture at any depth, and show the depth of penetration of seasonal rainfall. Their use brings about a most valuable economy in soil sampling, since this is no longer needed for the following of soil moisture trends, but can be concentrated on the quantitative evaluation of the maximum and the minimum water content of the soil profile in each season. Such an economy of soil sampling is rendered essential by the high variability of soil moisture distribution in this extensive soil type. The variability under plantation coffee is much higher than that illustrated for fallow soils in Table 1. Under forest covers, whose water use is of critical importance in East African water-supply problems, the variation of soil moisture is even greater. While setting gypsum blocks near a boundary of natural bamboo forest and plantation cypress, the top 2 ft. of the soil profile were observed to be darkened by coarse organic matter. Sampling to this depth gave the results shown in Table 2, which gives the means and ranges of seven replications at three depths under each cover.

TABLE 2

Soil Moisture Content under Forest

Depth	*Cover*	*Range of values*	*Means* (±3·6%)
0–6 in.	Cypress	55·3 to 74·7%	62·0%
	Bamboo	55·2 to 99·0%	77·8%
6 in.–1 ft.	Cypress	50·0 to 65·1%	55·1%
	Bamboo	52·5 to 60·0%	55·6%
1 ft.–2 ft.	Cypress	46·2 to 54·8%	51·2%
	Bamboo	42·3 to 55·2%	56·2%

Analysis was by angular transformation. Differences of means required for significance are 7·2 per cent. at P 0·05 and 9·7 per cent at P 0·01. The error of determination of moisture in each sample was very small, and no significant differences were observed between types of sampling tools. Approximately twice as many samples would have been required to reduce the significant difference between means to 5 per cent. at the P 0·05 level. Under these conditions it does not seem probable that sufficient calibrated blocks could be installed and maintained for quantitative estimation, but their use to indicate the most appropriate dates of sampling is of even greater importance.

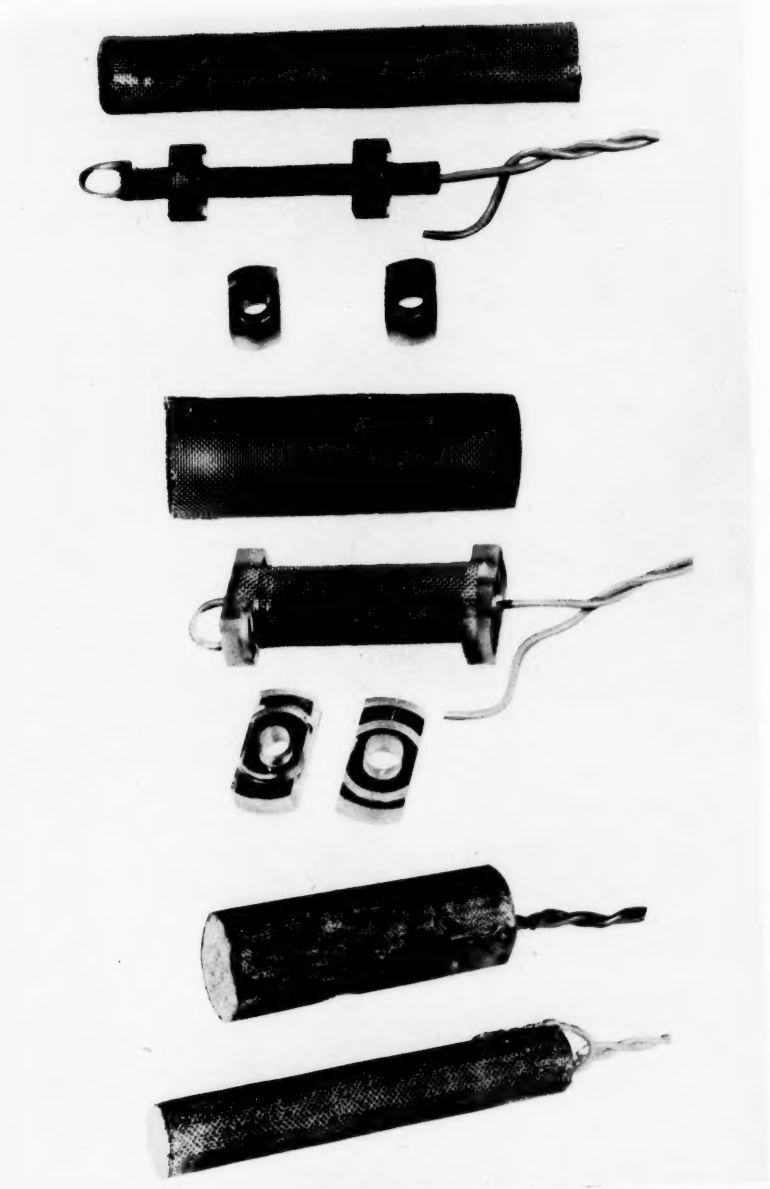
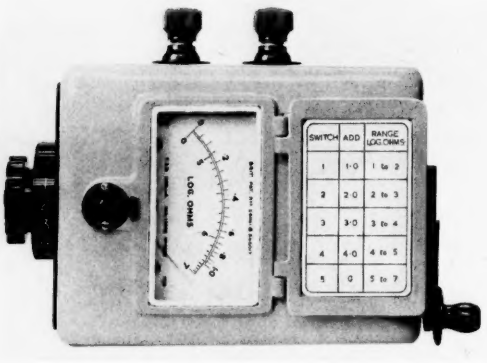
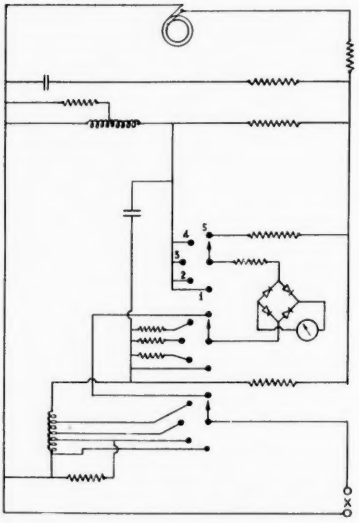


FIG. 3.

H. C. PEREIRA





Range	*Scale*	*Max. volts applied to X*
1	10–100 ohms	0·5 V.
2	100–1,000 ohms	1·6 V.
3	1,000–10,000 ohms	5·0 V.
4	10,000–100,000 ohms	16·0 V.
5	0·1–10 megohms	75·0 V.

120 r.p.m. of generator handle corresponds to 50 c./s. per sec.

FIG. 4

Root ranges are as yet inadequately explored for African vegetation, but for coffee the depth is approximately 15 ft. (Nutman, 1933; Rayner, 1945), while for Kikuyu grass (*Pennisetum clandestinum*), which is dominant on the wetter phases of Kikuyu Red Loam, the roots have recently been traced to a depth of 18 ft. Sets of gypsum blocks throughout these root ranges indicate the most appropriate dates for heavy programmes of soil sampling. Under dry conditions they materially reduce the number of replicate samples required, both by their quantitative interpretation and by their indication of the attainment of wilting tensions, at which soil horizons are brought to known moisture contents.

Summary

A cylindrical gypsum resistance block with concentric electrodes, suitable for placement by auger in deep subsoils, is described. A hand-operated dynamo and resistance meter suitable for use by native field staff is illustrated. The range over which quantitative results may be obtained in an extensive local type of lateritic soil is shown and the use of the technique is briefly discussed.

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PHOSPHATE FIXATION BY CLAY MINERALS*
MONTMORILLONITE AND KAOLINITE

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FIXATION of phosphate by soils, clays, and clay minerals has long been recognized. Differences of opinion have, however, been expressed regarding the manner in which phosphate is retained by these systems. Two theories have been proposed to explain the mechanism of the reaction. According to the first (1–7) the fixation of phosphate is mainly due to its precipitation by iron, aluminium, or calcium present in the systems. The second theory (8–16), on the other hand, holds that adsorption or anion exchange plays the prominent role in phosphate fixation. In the light of more recent investigations it is rather difficult to distinguish between the phosphate fixation by chemical precipitation and adsorption. It appears, however, that mutually contradictory or insufficient data have been obtained by various investigators on several points. These are: (i) whether kaolinite has any phosphate-fixing capacity (13–15, 17, 18); (ii) which of montmorillonite or kaolinite has the higher phosphate-fixing capacity (6, 7, 14); and (iii) how far particle size determines the phosphate-fixing capacity. The present investigation has been undertaken with a view to having fuller information on these points. In addition, the effects of (i) free inorganic oxide and (ii) the time of interaction of phosphate fixation have also been studied.

For this purpose estimation has been made of the amounts of phosphate adsorbed by (i) hydrogen kaolinite and hydrogen montmorillonite using different concentrations of phosphoric acid and over a wide range of reaction (pH), (ii) hydrogen systems prepared from the sub-fractions isolated from the entire clay fractions of montmorillonite and kaolinite, and (iii) hydrogen montmorillonites both before and after removal of free inorganic oxides from them. The effect of time on the adsorption of phosphates by hydrogen kaolinite and hydrogen montmorillonite has also been studied.

Experimental

Preparation of sub-fractions

The sub-fractions were prepared from the entire clay fractions isolated from a kaolinite and a montmorillonite by controlled centrifugal subsidence following the method of Baver and Whit (19) with the aid of a Sharples supercentrifuge. The depth of sampling and the rate of revolution of the centrifuge were kept constant and only the rate of feed, or the quantity of effluent per minute, was varied.

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Preparation of hydrogen kaolinite and hydrogen montmorillonite

The entire clay fractions, as also the different sub-fractions, were leached with 0·03N hydrochloric acid till all the exchangeable bases were removed, washed free from acid, and suspended in conductivity water.

Determination of base-exchange capacity

Base-exchange capacities were determined by potentiometric titration with bases using a Tinsley vernier potentiometer (type 3126) reading up to 0·01 m.v. and a Hartman and Braun galvanometer with a critical damping resistance of 22×10^4 ohms and having a current sensitivity of $4{\cdot}2 \times 10^{-11}$ amp. A hydrogen electrode in conjunction with a saturated calomel half-cell has been used.

Estimation of phosphorus

Phosphorus was estimated according to the method of Truog and Meyer (20). The extinction coefficient of the blue solution obtained on the addition of sulphuric acid-molybdic acid mixture to the phosphate solution followed by reduction with stannous chloride was determined with the help of a Haensch Schmidt spectrophotometer using a wavelength of 520 A. The extinction coefficients obtained with phosphoric-acid solutions of different known concentrations show that the intensity of the blue colour developed is proportional to the concentration of phosphorus in solution.

Definite amounts of a solution of phosphoric acid of known concentration were added to about 0·5 g. of hydrogen kaolinites or hydrogen montmorillonites, the final volume in each case was made up to 50 c.c. with distilled water, and allowed to stand for 4 days with occasional shaking, then filtered and an aliquot part of the clear filtrate was taken for phosphorus estimation. The extinction coefficient was determined as before, and from the graph obtained with phosphoric acid solutions of known concentrations the phosphorus content of the filtrate was calculated. The amounts of phosphorus adsorbed have been calculated from the difference between the phosphate contents of the added phosphoric-acid solutions and those of the corresponding clear filtrates.

Description of the mineral	*Ref. no. of sub-fractions*	*Ref. no. of corresponding hydrogen system*	*Average equivalent spherical diameter (in micron)*
Bentonite* from Kashmir	1	H—M_1	1·1
	3	H—M_3	0·10
	5	H—M_5	<0·05
	Entire	H—M	<2·0
Kaolin from Singbhum	1	H—K_1	1·1
	4	H—K_4	0·09
	Entire	H—K	<2·0

* X-ray analysis of the clay fraction isolated from the Kashmir bentonite shows that it is practically pure montmorillonite. The hydrogen systems prepared from the entire clay and the sub-fractions of this bentonite have been referred to in this paper as hydrogen montmorillonites.

Removal of free inorganic oxides

Free inorganic oxides were removed, using sodium sulphide, oxalic acid, ammonia, and hydrochloric acid (21).

The particulars of the clay minerals and their sub-fractions used in this work are given above.

Effect of Concentration of Phosphoric Acid in Solution on Phosphate Fixation

Phosphate fixation from increasing concentration of added phosphoric acid solutions by hydrogen kaolinite and hydrogen montmorillonite prepared from the entire clay fractions of the minerals is shown in Tables 1 and 2. The equilibrium pH values have also been recorded.

TABLE 1

Effect of Concentration of Added Phosphoric Acid on the Fixation of Phosphate by Hydrogen Kaolinite

Base-exchange capacity of H-kaolinite, 8·0 m.e. per 100 g. Time of interaction, 96 hours

Concentration of added H_3PO_4 (in normality)	*Weight (in g.) of H-kaolinite taken for each experiment*	*Equilibrium pH of the mixture*	*Amount of phosphate adsorbed. Milli-equivalents per 100 g. oven-dried colloid*
0·11	0·42	1·97	267·4
0·011	0·42	2·73	42·4
0·002	0·42	3·42	15·9

TABLE 2

Effect of Concentration of Added Phosphoric Acid on the Fixation of Phosphate by Hydrogen Montmorillonite

Base-exchange capacity of H-montmorillonite, 94·0 m.e. per 100 g. Time of interaction, 96 hours

Concentration of added H_3PO_4 (in normality)	*Weight (in g.) of H-montmorillonite taken for each experiment*	*Equilibrium pH of the mixture*	*Amounts of phosphate adsorbed, m.e. per 100 g.*
0·11	0·42	1·92	127·5
0·011	0·42	3·0	26·1
0·002	0·42	3·50	13·0

The data recorded in Table 1 show that H-kaolinite has quite an appreciable phosphate-fixing capacity. The amount of phosphate adsorbed per 100 g. of oven-dried material increases from 15·9 m.e. to 267·4 m.e. with an increase in the concentration of added phosphoric acid from 0·002N to 0·11N. It appears, therefore, that Midgley (17), as also Mukherjee and Raychaudhury (18), most probably worked with kaolinites having very coarse particles and hence failed to observe any appreciable phosphate fixation as suggested by Perkins and King (22).

It will be seen from Table 2 that H-montmorillonite can also adsorb phosphate. The amount of phosphate fixed per 100 g. of oven-dried colloid increases from 13·0 m.e. to 127·5 m.e. as the concentration of added phosphoric acid increases from 0·002N to 0·11N.

Phosphate Fixation and Reaction pH

A comparison of the data cited in Table 1 with those in Table 2 shows that at equal concentrations, especially at higher ones of added phosphoric acid, hydrogen kaolinite adsorbs more phosphate than hydrogen montmorillonite though the base-exchange capacity of the latter is many times greater than that of the former. The equilibrium pH values of the mixtures are, however, below 4·0 in every case. In view of Coleman's (6) observation that H-montmorillonite adsorbs as much, if not more, phosphate as H-kaolinite above pH 5·0, it was thought desirable to study the effect of the reaction (pH) on the phosphate fixation by H-montmorillonite and H-kaolinite. The results obtained with H-montmorillonite prepared from the finest fraction and the H-kaolinite prepared from the entire clay fraction are shown in Tables 3 and 4.

TABLE 3

Effect of pH on Phosphate Fixation by H-*Kaolinite*

Base-exchange capacity, 8·0 m.e. per 100 g. Concentration of added H_3PO_4, 0·1 N.; pH adjusted by addition of requisite amounts of NaOH. Time of interaction, 96 hours.

Initial pH of mixture	*Equilibrium pH of the mixture*	*Weight (in g.) of* H-*kaolinite taken for each experiment*	*Amount of phosphate adsorbed, m.e. per 100 g.*
3·0	2·56	0·42	309·7
5·0	4·45	0·42	218·3
7·0	6·66	0·42	126·1
9·0	8·25	0·42	22·7

TABLE 4

Effect of pH on the Fixation of Phosphate by H-*Montmorillonite*

Base-exchange capacity, 106 m.e. per 100 g. Concentration of added H_3PO_4, 0·11 N.; pH adjusted by addition of requisite amounts of NaOH. Time of interaction, 96 hours.

Initial pH of mixture	*Equilibrium pH of the mixture*	*Weight (in g.) of* H-*montmorillonite taken for each experiment*	*Amount of phosphate adsorbed, m.e. per 100 g.*
3·0	2·58	0·46	157·7
5·0	4·50	0·46	147·2
7·0	6·60	0·46	73·6
9·0	8·20	0·46	43·7

The amounts of phosphate adsorbed by H-kaolinite and also by H-montmorillonite decrease with an increase in the pH of the mixture, the decrease being more pronounced in the case of H-kaolinite. For example, it decreases from 309·7 m.e. to 22·7 m.e. per 100 g. of H-kaolinite as the pH rises from 3·0 to 9·0 while with H-montmorillonite from 157·7 m.e. to 43·7 m.e. The fixation of phosphate, as also the observed decrease in phosphate fixation with increasing pH, may be due to either of the two mechanisms: (i) phosphate fixation is due to a reversible exchange between phosphate ion in solution and the hydroxyl ions of the crystal lattice. These hydroxyl ions may be looked upon as the primarily adsorbed anions in the light of Mukherjee's theory (23). As the hydroxyl ion concentration in solution increases the above reversible reaction is more and more hindered, resulting in a progressive decrease in phosphate fixation; (ii) phosphate fixation is due to its precipitation as insoluble iron and aluminium phosphate. As the pH rises the activity of iron and aluminium for fixing phosphate is gradually reduced and consequently the amount of adsorbed phosphate decreases.

Considerations of the structural arrangement of the hydroxyl ions in the kaolinite crystals suggest that mechanism (i), viz. the reversible exchange between the phosphate ion in solution and the hydroxyl ions of the crystal lattice, may account for the high phosphate-fixing capacity of kaolinites and its enormous decrease with increasing pH. According to Pauling (24) and Gruner (25) kaolinite has an unsymmetrical layer lattice structure. Each packet consists of a sheet of hexagonal hydroxyl ions in octahedral arrangement with aluminium ions in their interstices (gibbsite sheet) fused on one side only with tetrahedral silica layers whose oxygen atoms are also spatially arranged in hexagonal form. The fusion takes place through the vertical oxygen atoms of the tetrahedra. These oxygen atoms are common both to the octahedral and tetrahedral layers. Thus the kaolinite packet has on one side a plane of oxygen ions in hexagonal arrangement and on the other a plane of closely packed hydroxyl ions. These hydroxyl ions on the surfaces of the crystals, which are also their cleavage planes, are available for exchange with phosphate ions.

The high phosphate fixation by H-montmorillonite observed in the present work, as also that reported by others, cannot be accounted for from a consideration of the arrangement of hydroxyl ions in montmorillonite crystals. Unlike kaolinite, montmorillonite has a symmetrical structure. Each packet is composed of an octahedral gibbsite layer fused on both sides with tetrahedral silica layers and consequently each face of the packet has a sheet of oxygen ions. The remaining hydroxyl ions of gibbsite sheet lying below the centre of the superposed hexagonal ring of oxygen ions, though available for exchange with ions of diameter smaller than oxygen, lie inaccessible to larger ions like the tetrahedral phosphate ion. Mechanism (ii), viz. phosphate fixation due to its precipitation as insoluble phosphates, probably plays the prominent role in this case. The hydroxyl ions present at the edges and corners of montmorillonite crystals as also exchangeable-aluminium ions present

on the surface of H-montmorillonites are, however, available for exchange with phosphate ions. This point is further discussed on p. 230.

A comparison of the data presented in Table 3 with those in Table 4 shows that in acid region H-kaolinite adsorbs more phosphate than H-montmorillonite, and with increasing pH the relative difference in the phosphate-fixing capacities of the two minerals gradually diminishes until in the region of pH 7·0 to 9·0 the order is reversed. The reversal in the phosphate-fixing capacity of the two minerals is rather significant. Coleman (6) observed a similar reversal between pH 3·0 and 7·0. It has been suggested (6) that more phosphate is adsorbed by H-montmorillonite than H-kaolinite. The greater fixation by H-kaolinite at pH 3 has been considered to be due to the greater activity of its iron and aluminium. In fact, he observed that the iron and aluminium in H-kaolinite are more soluble than the iron and aluminium in H-montmorillonite at pH 3·0. With a view to studying whether the greater phosphate fixation by H-kaolinite compared to that by H-montmorillonite at the acid region observed in the present work is due to the greater solubility of iron and aluminium present in H-kaolinite, about 0·5 g. of the minerals was shaken with 50 c.c. 0·1N HCl adjusted to pH 3·0 with NaOH, filtered after allowing to stand overnight, and then leached with additional 100 c.c. of HCl in 50-c.c. lots. Iron and aluminium dissolved from the minerals have been estimated in the total leachates as mixed oxides. The results are presented in Table 5.

The data presented in Table 5 show that the findings of Coleman (6), viz. that the iron and aluminium in kaolinitic clays are more soluble than the iron and aluminium in montmorillonitic clays, could not be verified with the H-kaolinite and H-montmorillonite used in the present work. They also indicate that the greater phosphate fixation in acid region by H-kaolinite compared to H-montmorillonite cannot be attributed to the greater activity of the iron and aluminium in kaolinite.

TABLE 5

Amounts of Iron and Aluminium dissolved from H-*Montmorillonite and* H-*Kaolinite by 0·1N HCl adjusted to pH 3·0*

System	*Weight in g. taken for each experiment*	*Iron and aluminium dissolved expressed as g. of mixed oxide per 100 g. of minerals*
H-montmorillonite (finest fraction)	0·46	0·87
H-kaolinite	0·46	0·13

Influence of Particle Size on Phosphate Fixation

Coleman (7) carried out phosphate fixation studies with hydrogen clays prepared from fine fractions ($< 0{\cdot}2\mu$) and coarse fractions (2·0 to $0{\cdot}2\mu$) isolated from a sandy loam and a clay loam having respectively kaolinite and montmorillonite as their dominant clay minerals. He found that the coarse clay fixed about one-half as much phosphate as the fine clay and that all of the phosphorus held by the coarse clay and

most of the phosphorus held by the fine clay are fixed by the free inorganic oxides. Opinions (17) have also been expressed that kaolinite fixes only small amounts of phosphate unless it is finely ground. In the light of these observations phosphate-fixation studies have been made with three sub-fractions of H-montmorillonite and two sub-fractions of H-kaolinite. The data are presented in Table 6.

It will be seen that at the lowest concentration (0.002N) of H_3PO_4 the H-montmorillonite prepared from the coarsest fraction fixes as much phosphate as that prepared from the finest one. At the highest concentration (0.11N) of the acid the increase in the phosphate fixation with decreasing particle size is, however, very marked, the amount of phosphate adsorbed by the coarsest fraction of montmorillonite being about one-fourth of that adsorbed by the finest fraction. The base-exchange capacity (b.e.c.) also increases from 80 m.e. to 106 m.e. per 100 g. With hydrogen kaolinites only the highest concentration of H_3PO_4 has been used. The phosphate-fixation capacity has been found to increase from 99·7 m.e. to 140·3 m.e. per 100 g., while the b.e.c. increases from 4·0 m.e. to 15·0 m.e. per 100 g. It is significant to note that even the coarsest fraction of kaolinite has quite an appreciable phosphate-fixing capacity.

In the case of hydrogen kaolinites the increase in phosphate fixation with decreasing particle size may be accounted for by the increase in the availability of hydroxyl ions due to an increase of specific surface. With montmorillonites this increase may be due to either (i) an increasing accumulation of free inorganic oxides with decreasing particle size, or (ii) an increase in the number of hydroxyl ions present on the edges and corners of montmorillonite crystals or of exchangeable-aluminium ions present on the surface of H-montmorillonites. This point is further discussed on p. 231.

TABLE 6

Hydrogen clays	*Average equivalent spherical diameter (in microns)*	*M.e. of phosphate adsorbed per 100 g. at H_3PO_4 concentration of*			*Base exchange capacity per 100 g.*
		0·11N	*0·011N*	*0·002N*	
H—M_1	1·1	48·4	21·7	13·3	80
H—M_3	0·10	115·2	25·2	12·6	95
H—M_5	<0·05	180·5	27·4	13·7	106
H—K_1	1·1	99·7	..	..	4·0
H—K_4	0·09	140·3	..	..	15·0

Relation between Phosphate Fixation by Clays and Free Inorganic Oxides present in them

It has been reported by various investigators (4, 5, 6, 7) that the free iron and aluminium oxides are mainly responsible for the phosphate fixation by hydrogen montmorillonites. The effect of the removal of the free inorganic oxide on the phosphate fixation has therefore been studied, using hydrogen montmorillonites prepared from the coarsest and the finest fractions. Their base exchange capacities have also been

determined after the removal of the free sesquioxide by potentiometric titration with NaOH. The following data have been obtained.

TABLE 7

Phosphate Fixation by H-*Montmorillonite before and after Removal of Free Inorganic Oxides contained in it*

M.e. phosphate adsorbed per 100 g.

	Concentration of added H_3PO_4					
	*0·11*N		*0·011*N		*B.e.c., m.e. per 100 g.*	
System	*Before treatment*	*After treatment*	*Before treatment*	*After treatment*	*Before treatment*	*After treatment*
H—M_1	48·4	Negligible	21·8	n.d.*	80	82·0
H—M_5	180·4	80·1	27·4	16·0	106	60·0

* Not determined.

The data reported in Table 7 show that all of the phosphate held by the coarsest fraction is fixed by the free iron and aluminium oxide. The base-exchange capacity remains practically unaltered on the removal of the sesquioxide, indicating that treatment according to Truog's method has not brought about any decomposition of the adsorption complex. A comparison of the b.e.c. before and after removal of free oxides indicates that only traces of free oxide are most probably present in the coarsest fraction. This amount, while having very little influence on the b.e.c., appears to have a pronounced effect on the phosphate fixation. The phosphate-fixation capacity of the finest fraction, on the other hand, is reduced to about one-half of its original value on the removal of the free oxides. The b.e.c. of this fraction also decreases from 106 m.e. to 60 m.e. per 100 g., indicating a decomposition of the adsorption complex. The diminution in phosphate-fixing capacity may thus arise either from (i) the removal of free inorganic oxides, or (ii) a decomposition of the complex, or due to both (i) and (ii).

The observed phosphate fixation by hydrogen montmorillonite prepared from the finest fraction even after the removal of the free inorganic oxides from it is most probably due to the existence of sufficient hydroxyl ions at the edges and corners of montmorillonite crystals as also of exchangeable-aluminium ions present on the surface of H-montmorillonites. The number of such ions will increase with decreasing particle size, and hence the finest fraction can fix a considerable quantity of phosphate even when the free oxides are removed from it.

It has been observed (7) that phosphate-fixation by kaolinites and montmorillonites is influenced by reaction pH only as long as the free oxides are not removed. The results obtained in the present investigation, however, show (Table 8) that the effect of pH on the fixation of phosphates by the finest sub-fraction of H-montmorillonite persists even after the removal of the free sesquioxides from it. The corresponding data obtained before the removal of free oxides are also included for comparison.

TABLE 8

Effect of pH on Phosphate Fixation by H-*montmorillonite before and after the Removal of the Free Inorganic Oxides contained in it*

Concentration of phosphoric acid used, 0·11N pH adjusted by adding requisite amount of NaOH.

M.e. phosphate adsorbed per 100 g. at			
pH 9		*pH* 1·9	
Before treatment	*After treatment*	*Before treatment*	*After treatment*
43·7	22·9	180·5	80·4

The Effect of Time of Interaction between Soluble Phosphates and Hydrogen Minerals on Phosphate Fixation

In view of the heterogeneous character of the interaction between phosphoric acid and hydrogen kaolinites and hydrogen montmorillonites, the effect of time on phosphate fixation has been studied. It has been observed (Table 9) that the amount of phosphate fixed increases with time. The increase is very marked in the case of the coarsest fraction of H-montmorillonite. It has already been discussed on p. 231 that in this fraction all of the phosphorus is held by the inorganic oxides. It may be assumed therefore that on the addition of phosphoric acid the free iron and aluminium oxide first come into solution and then are precipitated as insoluble phosphates.

TABLE 9

Effect of Time of Interaction on Phosphate Fixation

Concentration of phosphoric acid used, 0·11N

Time allowed for interaction	*M.e. phosphate adsorbed per 100 g. of*		
	H-*kaolinite* (*entire*)	H-*montmorillonite* ($H—M_5$)	H-*montmorillonite* ($H—M_1$)
4 days	267·4	180·5	48·4
30 ,,	315·5	200·2	135·1

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A STUDY OF VARIOUS FRACTIONS OF THE MANGANESE OF NEUTRAL AND ALKALINE ORGANIC SOILS

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In a study of various manganese fractions of soils Heintze and Mann (1949) showed that manganese added to alkaline organic soils was not readily recovered in subsequent extractions with neutral M-ammonium acetate. As a result of the investigation the hypothesis was put forward that manganese deficiency occurring on alkaline organic soils with appreciable total manganese contents was due to the formation of complexes of divalent manganese with the organic matter. Leeper (1935, 1940, 1947) suggested that the highly reactive manganese defined as the fraction which dissolves in 0·2 per cent. hydroquinone in neutral M-ammonium acetate may be potentially readily available, and found this value helpful in characterizing manganese-deficient soils. He further distinguished between highly and moderately reactive forms of higher oxides of manganese by their behaviour under different reducing conditions. Dion, Mann, and Heintze (1947) recovered 80 per cent. of commercial manganese dioxide or pyrolusite added to a marsh soil by extraction with 0·2 per cent. hydroquinone in M-ammonium acetate, but only 10 per cent. of added manganite and none of added hausmannite.

Heintze and Mann (1949) found that hydroquinone-soluble manganese formed a smaller fraction of the total manganese in highly organic soils than in mineral soils. This result could indicate that in some organic soils the higher oxides of manganese occurred in a less reactive form than those present in mineral soils. The lower values could, however, also be interpreted as the result of retention by the organic matter of the divalent manganese produced from readily reducible manganese oxides.

The present work is an attempt to find out if, and how far, these alternatives can be differentiated.

Materials and Methods

Soils. The soils were chosen to give a series with a wide range of organic-matter content and were, with one exception, either neutral or alkaline. Several samples of some of these soils had to be taken during the course of the work, and the values given for the same manganese fraction of one soil may vary in the different experiments. The variations were not sufficiently great to affect the conclusions reached.

Pyrolusite, hausmannite, and manganite. The samples of the minerals used—pyrolusite (MnO_2) and hausmannite (Mn_3O_4) from Ilmenau, and manganite (MnO(OH)) from Ilfeld, Harz—were obtained from the Mineral Department of the British Museum. They were ground in a mechanical agate mortar for 3 to 4 hours before use.

Soil nitrogen was determined by a micro-Kjeldahl procedure using Markham's (1942) still.

Soil organic carbon was estimated by the method of Walkley and Black (1934).

Manganese determinations. The manganese in all extractions was determined colorimetrically after conversion to permanganate with sodium periodate. Except where otherwise stated, an extraction time of 1 hour was used and a soil : solution ratio of 1 : 20. The soils were extracted either in flasks with mechanical shaking or in beakers with intermittent stirring. The latter method was adopted to facilitate the maintenance of the reaction at pH 7 during the extraction, by addition of M-acetic acid or M-ammonium hydroxide as required.

Total manganese was determined colorimetrically, as above, after fusion of the soil with sodium carbonate and removal of the silica.

Exchangeable manganese was estimated by extraction with M-ammonium acetate.

Hydroquinone-soluble manganese was estimated by extraction with M-ammonium acetate containing various concentrations of hydroquinone as stated in the text.

Hydrosulphite-soluble manganese was estimated by extraction with M-ammonium acetate containing various concentrations of sodium hydrosulphite as stated in the text.

Iron was determined colorimetrically with $\alpha\alpha'$ dipyridyl.

Calcium was determined volumetrically as calcium oxalate.

Results

Hydroquinone-soluble manganese of soils

The values of hydroquinone-soluble manganese for the series of soils given in Table 1 were obtained by shaking the soils for 1 hour with neutral M-ammonium acetate containing 0·2 per cent. hydroquinone. In subsequent experiments the extractions were carried out in beakers with intermittent stirring for 1 hour, the suspensions being maintained at pH 7. In Table 1 the soils are set out in order of increasing organic-carbon contents. In general the hydroquinone-soluble fraction of the total soil manganese decreases as the organic-matter content of the soil increases.

Heintze and Mann (1949) showed that when divalent manganese in M-ammonium acetate at pH 7 was added to neutral or alkaline organic soils a large part of the manganese was retained by the soils in a form not readily exchangeable. The presence of hydroquinone does not prevent retention, as is shown by the results, in Table 2, of experiments to test uptake of divalent manganese by a number of soils in presence of M-ammonium acetate at pH 7 with and without hydroquinone. Manganese sulphate was added to the ammonium-acetate solution to give 220 or 1,100 parts Mn per million soil, and the amounts remaining in solution overnight with and without 0·2 per cent. hydroquinone were determined. Parallel estimations of the hydroquinone-soluble manganese fractions of the soils were also made. In general the added manganese left in solution with hydroquinone present did not exceed that in the absence of

TABLE 1

Relation between Organic-matter Content and Hydroquinone- and Hydrosulphite-manganese Fractions of Soils

Soil	*pH*	*Organic Carbon (mg./g. soil)*	*Nitrogen (mg./g. soil)*	*Total Mn p.p.m.*	*Hydro-quinone-Mn p.p.m.*	*% Total*	*Hydro-sulphite-Mn p.p.m.*	*% Total*
Gold Coast .	6·0	1·6	0·26	2,320	1,530	66	1,530	66
Barnfield 8:0 .	8·2	6·5	1·00	1,400	960	68	880	63
6821 . .	8·2	8·4	1·07	273	137	50	192	70
Felstead . .	7·4	10·8	1·62	686	376	55	384	56
Spalding . .	7·8	11·7	1·54	400	172	43	196	49
6802 . .	8·1	13·5	1·86	945	400	42	430	46
Barnfield 1:0 .	8·0	21·6	2·70	1,400	432	31	416	29
Hampshire .	8·0	21·9	2·94	332	106	32	168	50
Kent 1 . .	7·9	30·6	4·20	328	122	37	170	52
Ivychurch .	7·6	31·8	4·20	328	106	32	120	37
7080 . .	7·5	37·8	4·35	477	74	16	130	27
Allotment .	7·6	39·0	3·40	1,560	344	22	400	26
Isleham . .	7·2	135·0	8·74	163	16	10	42	26
7085 . .	7·1	137·5	12·00	178	24	14	50	28
7406 . .	7·6	192·0	15·30	320	72	22	148	46
Burwell . .	7·2	200·0	16·20	480	57	12	138	29
Swaffham .	7·2	243·0	20·00	565	76	13	132	23
Methwold .	7·6	248·0	22·00	840	180	21	236	28

TABLE 2

The Effect of Hydroquinone (0·2%) on the Uptake by Soils of Manganese added as Sulphate in Solutions of M-Ammonium Acetate

The values given are corrected for hydroquinone-soluble manganese of the soils.

Soil	*Manganese (p.p.m.)*		
		Taken up by the soil	
	Added	*Hydroquinone absent*	*Hydroquinone present*
6821 . . .	220	24	12
	1,100	280	236
7080 . . .	220	100	110
	1,100	680	714
Isleham . .	220	148	148
	1,100	680	656
7085 . . .	220	144	140
7406 . . .	220	152	156
Swaffham . .	220	160	132

hydroquinone by an amount widely different from the hydroquinone-soluble fraction of the soil manganese.

If hydroquinone-soluble manganese is determined on soil samples previously extracted with M-ammonium acetate in determining exchangeable manganese the results are frequently less than those obtained by extracting the soil directly with ammonium acetate and hydroquinone.

In organic soils the previous extraction by ammonium acetate alone may reduce the hydroquinone-soluble manganese by one-half. If soils take up Mn^{++} by cationic exchange, the prior replacement of Ca^{++} by NH_4^+ would be expected to increase the amounts of Mn^{++} adsorbed by the soil. The effects of prior removal of exchangeable calcium could be balanced by adding an equal quantity of a calcium salt to the ammonium-acetate solution containing hydroquinone (Table 3).

TABLE 3

The Effect of Preliminary Extraction of Soils with M-Ammonium Acetate on the Manganese subsequently dissolved at pH 7 by M-Ammonium Acetate containing 0·2% Hydroquinone, with and without Calcium (as Calcium Nitrate) equal to that removed in the Preliminary Extraction

Soil	Total manganese (p.p.m.)	Hydroquinone-soluble manganese (p.p.m.)		
		Control soil	Soil previously extracted	
		No previous treatment	Calcium not restored	Calcium restored
Barnfield 8:0	1,400	930	880	..
Barnfield 1:0	1,400	424	384	..
Allotment	1,560	368	324	392
Isleham	163	20	5	30
7085	178	22	11	..
7406	320	72	40	74
Swaffham	565	76	48	80
Burwell	480	66	64	65
Methwold	840	187	132	210

Heintze and Mann (1949) found that cadmium, copper, cobalt, nickel, or zinc salts added to the ammonium acetate used for soil extractions at concentrations of 0·02–0·04 N were more effective than additions of calcium salts, both in the extraction of exchangeable manganese and in preventing the uptake of added divalent manganese by soils. Experiments were therefore made to find out if the hydroquinone-soluble manganese could be similarly increased by adding salts of divalent cations to the ammonium acetate and hydroquinone. The effect of varying the soil:solution ratio was also tested. The results are set out in Table 4. Neither salt addition nor dilution altered the hydroquinone-soluble manganese fraction appreciably in a mineral soil with low organic-matter content. In some soils with high organic-matter content large increases of this fraction were produced both by increasing the soil:solution ratio and by adding cadmium, copper, cobalt, nickel, or zinc salts. Thus the value of the hydroquinone-soluble manganese of the Methwold fen soil was increased from 180 to 560 p.p.m., i.e. to 68 per cent. of the total soil manganese. With other soils, however, the final values were not as high and rarely exceeded 30 per cent. of the total soil manganese. The values for the hydroquinone-soluble manganese could also be increased by using ammonium-acetate solutions at pH 5·3, where, as shown by Dion *et al.* (1947), hausmannite and manganite are only slightly reduced. It is clear from the results that the low values obtained

TABLE 4

Effect of Variation in the Soil: Solution Ratio and of Various Salts at a Concentration of 0·02 N on the Extraction of Manganese from Soils by M-Ammonium Acetate containing 0·2% Hydroquinone

	Manganese p.p.m.					
	Barnfield 8:0		*Allotment*		*Methwold*	
Total Mn.	1400		1560		840	
Soil: solution ratio	1:20	1:100	1:20	1:100	1:20	1:100
Addition						
O	960	1,050	408	710	180	280
$CaCl_2$	980	1,100	448	740	216	296
$MgSO_4$	975	1,050	..	690	232	..
$CuSO_4$	1,040*	1,050*	600	760	296	440
$CdCl_2$	..	..	568	820	292	395
$CoCl_2$	..	..	..	..	324	560
NiAc	980	980	560	810	300	500
$ZnSO_4$	960	1,100	544	760	345	485

* 0·01 N-$CuSO_4$

for hydroquinone-soluble manganese of organic soils are, at least in part, due to retention of divalent manganese by the soil organic matter. To investigate how far variations in reducibility of the manganese higher oxides are also concerned, hydrosulphite was used as a reducing agent instead of hydroquinone.

Reduction of pyrolusite, hausmannite, and manganite by hydrosulphite and hydroquinone

Dion *et al.* (1947) found that, while a sample of pyrolusite was readily reducible by hydroquinone in ammonium acetate at pH 7, samples of hausmannite and manganite were resistant to reduction under these conditions. Experiments have now been made to compare the reducing action of hydroquinone and hydrosulphite on these minerals. The results (set out in Table 5) show that hydrosulphite reduces hausmannite

TABLE 5

The Reduction of Hausmannite, Manganite, and Pyrolusite by varying Concentrations of Hydroquinone or Hydrosulphite in M-Ammonium Acetate at pH 7. Time = 1 hr.

	Manganese in solution (mg.)		
Addition	*Hausmannite* 3·7 mg. Mn.	*Manganite* 3·06 mg. Mn.	*Pyrolusite* 2·98 mg. Mn.
0·2% hydroquinone	0·06	0·42	2·97
1·0% ,,	0·16	0·43	2·97
2·0% ,,	0·25	0·52	2·90
0·4% hydrosulphite	0·79	1·83	2·82
1·0% ,,	1·14	2·46	2·86
2·0% ,,	1·19	2·46	2·86

and manganite much more readily than does hydroquinone, though the reduction of these minerals, unlike that of pyrolusite, was not complete in the experimental time, even when the hydrosulphite concentration was raised from 0·4 to 2 per cent.

Hydrosulphite-soluble manganese of soils

The values, given in Table 1, for the hydrosulphite-soluble manganese fractions of the soils were obtained by shaking the soils for 1 hour with neutral M-ammonium acetate containing 0·4 per cent. sodium hydrosulphite. Under these conditions, with the mineral soils of low organic-matter content the hydrosulphite-soluble manganese was in general little more than the hydroquinone-soluble manganese, but with the mineral soils of high organic-matter content and the organic soils it was, in general, much greater. In these estimations with hydrosulphite the final pH values of the reaction mixtures ranged from 6·5 to 6·7, whereas with hydroquinone the range was from 7·0 to 7·3. In experiments using concentrations of hydrosulphite higher than 0·4 per cent. a greater fall in pH was observed. In subsequent experiments, therefore, the extractions were carried out in beakers with intermittent stirring, and the suspensions were maintained at pH 7. Parallel experiments were made with hydroquinone and hydrosulphite, using a range of concentrations of each reductant. The results are shown in Table 6. Increase in hydrosulphite

TABLE 6

Manganese and Iron extracted at pH 7 from Soils by M-Ammonium Acetate containing Varying Concentrations of Hydroquinone, Hydrosulphite, or 1% Hydroxylamine

	Manganese and iron extracted (p.p.m.)							
	Allotment		*Isleham*		*Swaffham*		*Methwold*	
Total Mn. . .	1,560		163		565		840	
	Mn	Fe	Mn	Fe	Mn	Fe	Mn	Fe
Addition								
0·2% hydroquinone	320	Trace	16	Trace	78	Trace	182	Trace
0·4% ,,	348	,,	16	,,	74	,,	186	,,
1·0% ,,	384	,,	13	,,	68	,,	188	,,
1·0% hydroxylamine	432	,,	..	..	..	..	..	..
0·4% hydrosulphite	376	1,480	40	3,220	124	1,010	236	740
1·0% ,,	520	2,320	60	5,580	154	1,480	352	2,560
2·0% ,,	756	3,460	76	6,620	192	2,000	408	3,220

concentration from 0·4 to 2 per cent. produced increases of up to 100 per cent. in manganese extracted from soils of high organic-matter content. Little increase was found with mineral soils of low organic-matter content, where the greater part of the total manganese was extracted with 0·4 per cent. hydrosulphite. In the parallel experiments with hydroquinone little or no effect was produced by increasing the hydroquinone concentration with any of the soils tested. A few experiments were also made with hydroxylamine as reducing agent. Dion *et al.* (1947) found

that hydroxylamine gave results slightly higher than, but of the same order as, those given by hydroquinone. In experiments with the Allotment and Swaffham soils increases in hydroxylamine-hydrochloride concentration from 0·2 to 1 per cent. had little effect. The values obtained for hydroxylamine-soluble manganese were of the same order as those for hydroquinone-soluble manganese.

Since hydrosulphite has been postulated to extract higher oxides of manganese less reactive than those extracted by hydroquinone, and has been shown to be a more effective reductant of hausmannite and manganite than is hydroquinone, these results suggest that a larger part of the soil manganese was present in comparatively unreactive forms in the soils of high organic-matter content. In further investigations, however, it was found that hydrosulphite, under the conditions used, partially prevented the uptake by the organic soils of divalent manganese applied in ammonium acetate at pH 7. This is shown by the results set out in Table 7. The soil extracts made at pH 7 with ammonium acetate and

TABLE 7

The Effect of Varying Concentrations of Hydrosulphite on the Uptake at pH 7 by Soils of Manganese added as the Sulphate in Solutions of M-ammonium Acetate

The values given are corrected for the hydrosulphite-soluble manganese of the soils. Manganese added = 1,100 p.p.m.

Addition	*Manganese taken up by soil (p.p.m.)*			
	Barnfield 8:0	*Isleham*	*Swaffham*	*7406*
0	270	676	740	640
0·4% hydrosulphite .	150	468	672	375
1·0% ,,	..	328	518	350
2·0% ,,	..	280	460	190

hydrosulphite contained large amounts of iron. Extracts made in the same way with hydroquinone or hydroxylamine as reductant contained only traces of iron. In experiments (see Table 8) to test the effect of

TABLE 8

The Effect of Ferrous and Ferric Iron on the Uptake at pH 7 by Soils of Manganese added as the Sulphate in Solutions of M-ammonium Acetate

Addition	*Manganese added (p.p.m.)*	*Manganese in solution (p.p.m.)*		
		Swaffham	*7406*	*7085*
0	0	1	2	1
0·005 M-Fe^{++} . .	0	44	56	24
0·01 M-Fe^{++} . .	0	..	92	32
0	1,100	350	380	475
0·005 M-Fe^{++} . .	1,100	540	660	680
0·01 M-Fe^{++} . .	1,100	..	740	800
0·01 M-Fe^{+++} . .	1,100	380	430	460

ferrous and ferric iron on the uptake of added divalent manganese by soils in presence of ammonium acetate at pH 7, it was found that ferrous ammonium sulphate at concentrations of 0·01 and 0·02 N markedly diminished the uptake, whilst addition of ferric ammonium sulphate to ammonium acetate did not. Under the conditions used it is unlikely that the ferric iron remained in solution. Addition of ferrous ammonium sulphate in the estimation of hydroquinone-soluble manganese increased the amounts of manganese extracted. The increases produced were, however, only of the same order as the values for manganese extracted by adding ferrous ammonium sulphate alone to the ammonium acetate. Since raising the hydroquinone concentration had little effect on the amounts of manganese extracted, the increase in hydroquinone-soluble manganese produced by adding ferrous ammonium sulphate could be due to the previously observed effect of ferrous iron on the uptake of divalent manganese by the soil. But since hausmannite was found to be reduced by a mixture of hydroquinone and ferrous ammonium sulphate more strongly than by hydroquinone alone, the possibility cannot be excluded that, under the conditions used, ferrous iron reduces soil higher oxides of manganese not reduced by hydroquinone. The results show that differences in the amount of manganese extracted from organic soils by neutral ammonium acetate containing hydroquinone or hydrosulphite do not necessarily indicate differences in reactivity of the higher oxides of manganese of the soils. The higher values obtained for soil manganese extracted using hydrosulphite as reductant in place of hydroquinone might, at least in part, be explained by the effect of the iron brought into solution in preventing the uptake by the soil of the divalent manganese formed by reduction.

Discussion

The results of the present work show that with some organic soils low values for hydroquinone-soluble manganese in relation to the total soil manganese may be due to retention by the soil organic matter of the divalent manganese formed by reduction. Such manganese is not readily exchangeable with NH_4^+ or Ca^{++} ions. The values obtained are considerably increased by the use of hydroquinone in ammonium acetate solutions of lower pH value (5·3), where less manganese would be taken up by the organic matter as shown by Heintze and Mann (1949). In the extraction of the manganese fraction which is not readily exchangeable, mixtures of salts of copper, cadmium, cobalt, nickel, or zinc with ammonium acetate are far more effective than ammonium acetate alone. By use of these salts, particularly in conjunction with high soil : solution ratios in extraction, it was possible to raise the value of the hydroquinone-soluble manganese of an organic soil of high total manganese content to 60–70 per cent. of the total soil manganese. This value is of the same order as those obtained for the hydrosulphite-soluble manganese of mineral soils of high total manganese content and low organic-matter content. With other organic soils, however, while the use of these methods produces considerable increases in the hydroquinone-soluble manganese, the final values obtained may still be as low as 30 per cent.

of the total soil manganese. In some cases more manganese was extracted from these soils by the use of hydrosulphite in place of hydroquinone, though the values obtained were still low in comparison with those for mineral soils of high total manganese and low organic-matter content. In such soils the results may be due to the presence of relatively unreactive higher oxides of manganese. Thus while hausmannite and manganite were reduced more readily by hydrosulphite than by hydroquinone, the reduction of these minerals was not complete under the conditions used. At pH 7 hydrosulphite reduces ferric oxides of the soils whereas hydroquinone does not. It would therefore be expected that where higher oxides of manganese are coated with ferric oxides hydrosulphite would extract more manganese than hydroquinone. But analyses of concretions of manganese and iron oxides gave the same results for hydroquinone- and hydrosulphite-soluble manganese. It was shown by Heintze and Mann (1949) that manganese taken up by organic soils from solutions of manganopyrophosphate could not be recovered by subsequent extraction with hydrosulphite. It is possible, therefore, that part of the manganese not extracted from organic soils by hydroquinone or hydrosulphite under the conditions used may represent not unreactive higher oxides of manganese but manganese firmly bound in complexes with the organic matter.

Summary

1. In a series of neutral and alkaline soils with a wide range of organic-matter content the percentage of the total soil manganese extracted by neutral ammonium acetate containing 0·2 per cent. hydroquinone decreased with increase in soil organic matter.

2. Evidence was obtained that the low values for hydroquinone-soluble manganese with the soils of high organic-matter content were due, at least in part, to retention by the soil organic matter of the divalent manganese formed by reduction.

3. Under the conditions used the manganese minerals hausmannite and manganite were more readily reduced by sodium hydrosulphite than by hydroquinone.

4. The manganese extracted from organic soils by neutral ammonium acetate containing 0·4 per cent. hydrosulphite was generally greater than that if 0·2 per cent. hydroquinone was used. The interpretation of these differences is complicated by the effect of hydrosulphite on the retention of divalent manganese by the soil organic matter.

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ON pC, pS, AND pN AS INDICATING FUNCTIONS OF ELECTRICAL SOIL CONDUCTIVITY

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FOR many years the measurement of the electrical conductivity of water extracts or suspensions of soils has been widely employed as a guide to their electrolyte content, but the terms used to express the result have not been entirely satisfactory. The truth of this is seen in the several methods of expression employed in the many papers on the subject. To increase the difficulties of the reader there is diversity of opinion on the best soil : water ratio to use; and though this is not the main topic of this paper it should be mentioned, for the comparison of results is made more difficult by this uncertainty. One well-known text-book recommends a 1 : 5 ratio, believing that a good correlation with salt content is thereby obtained. Other workers prefer 1 : $2\frac{1}{2}$ or 1 : 1 or even a so-called saturation ratio.

Our desire is to draw attention to the varied ways in which the electrical conductivity is itself expressed in the literature and to suggest a manner and term of expression which is short, logical, appropriate, useful, and significant. We suggest that the term pC be used for the common co-logarithm of the specific conductivity of extracts or suspensions of soils. Not only does this term enable large numbers to be condensed (as do the analogous terms pH and pF), but some analytical and soil fertility relationships become clearer by using the pC notation. We also propose the term pS for the common co-logarithm of the salt concentration expressed as grammes weight per millilitre or p.p.m. $\times 10^{-6}$. This, when converted into a gramme-equivalent concentration as gramme-equivalents per litre, produces the third new term, pN, for the common co-logarithm of the normality as usually understood.

The first of these terms, namely pC, has been in use in the Soil Laboratory of the West of Scotland Agricultural College for nine years. It has found general acceptance among the Agricultural and Horticultural Advisory Staff on account of its significance in relation to soil fertility and amendments. Over 30,000 samples of soil have been examined for the conductivity of their aqueous suspensions. For all glasshouse soils pC values are reported to the Organizers as a routine measure.

We have often been pressed to give more precise details of the relation of pC to the salt concentration, but we have not felt it wise to quote exact figures in view of possible misunderstanding. Theoretical relationships do not provide quite the information desired. We have been content to await a sufficient accumulation of independent evidence which would enable us to be more precise. Thanks to much research by U.S. and other workers we now feel confident that it is possible to relate the pC values obtained in the laboratory to the practical values of salt

concentrations. We would refer to three U.S. publications in which the new terms may be compared.

Referring first to the paper by J. C. Wilcox, *Soil Science* (1948), **63**, 107–17, if p.p.m. are converted to pS and conductivity in mhos $\times 10^5$ to pC, a remarkable clarification occurs without the use of log-log paper. All the values representing the more concentrated solutions down to about 100 p.p.m. (i.e. pS 4) lie on a very good straight line; the remainder show an erratic distribution which may be due to disturbing effects of carbon dioxide at these concentrations. As an approximation, from these figures we can say pS = pC.

In the paper by R. B. Campbell, C. A. Bower, and L. A. Richards, of the U.S. Regional Salinity Laboratory, published in the *Proceedings of the Soil Science Society of America* (1948), **13**, 66–69, we see an excellent correlation (for the soils considered) between osmotic pressure, conductivity, and electrolyte concentration when the last is given in equivalent terms. This correlation is made clear in that journal by the use of log-log paper. We would use pF, pC, and pN to demonstrate at once the same significant correlations.

Combining these figures and those of Wilcox we find that the following approximate relations may be assumed to be sufficiently exact for general use:

$$pC = pS$$
$$pC = pN + 1{\cdot}17$$
$$pC = 5{\cdot}74 - pF$$

where:

S = p.p.m. $\times 10^{-6}$
C = mhos/cm.
N = normality of solution
$pF = 3 + \log_{10}$ osmotic pressure in atmospheres

In applying these formulae, a small correction may have to be made to suit the soil : water ratio employed, for pC is the negative logarithm of the conductivity of the soil extract or suspension in which the electrodes are immersed.

U.S. workers are largely using osmotic pressures, equivalent concentrations, and (direct) conductivities, and sometimes are differentiating two components of free energy into moisture and osmotic potentials. The value of their work is obscured by this differentiation. These usages are confusing and are difficult to correlate in physical terms. The confusion is largely of North American making, for the pF concept as originally expressed was perfectly general. Paul J. Kramer, *Plant and Soil–Water Relationships* (1949), p. 34, would appear to support Richards and Weaver (1944), *Journal of Agricultural Research*, **69**, 215–35, in rejecting pF, seeing no greater virtue in it than its ability to render numerical quantities compact. D. W. Thorne and H. B. Peterson in their recent book *Irrigated Soils* (1949) would reject pF on the grounds that it had been misunderstood and misapplied; yet they conclude (we quote): 'osmotic forces are often very great and the moisture tension and the osmotic tension must both be measured.' To quote again from

the same authors: 'In managing saline lands the total moisture tension may amount to only one atmosphere and apparently there would be ample available water present for plant growth, but the osmotic pressure might be 11 atmospheres, the permanent wilting point would be near, and the plants would be suffering from low water availability.'* Therefore we feel that the detractors of the pF term and concept have justified the need for it.

Our present interest in pF and, consequently, in our terms of pC, pS, and pN comes from the intimate relationship between electrolyte and osmotic effects. Our suggested new terms have all the well-known advantages shown by the strictly analogous terms of pF, pH, pK_a, pK_b, &c. These advantages depend not only upon the ease by which cumbersome numbers and 'difficult' curves can be accommodated but upon the observation that phenomena indicated by the terms appear to be the significant operating factors. This is demonstrable for pC in many available published papers, for example, in the graphical representation of two sets of figures from R. C. Reeve and others, Utah Agricultural Experiment Station Bulletin 335 (1948).

We take first the diagrams showing the salt content in soil depth following various leaching treatments for sites A and D (Reeve, Fig. 7 and Fig. 9). On redrawing these as depth/pC the two series appear to be more nearly related than do the original curves which, in fact, appear to obscure an existing relationship now brought out. In the same paper the somewhat diffuse facts shown in Reeve, Fig. 16, relating yields of grain to conductivity, when restated so that co-logarithmic (pC) means are plotted, show an almost straight line for site C, a slightly curved relation for site A lying almost over the line for site C, with that for site D anomalous but clearly differentiated. Other examples can be seen in Kramer's book.

These and similar relations, once elicited, are of considerable practical value. We have found, from many publications, that after logarithmic conversion in terms of pC (especially), relations of soil behaviour and crop yields to salt content and electrical conductivity are often direct. We do not claim to prove this, but we submit that the terms pC, pS, and pN demonstrate such facts more succinctly; we believe them to be fundamental functions. The advantages of the terminology proposed are clear, and we trust that the terms will be accepted, especially pC, which appears to be most generally useful.

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* Nevertheless, in the definition of wilting-point (pp. 32, 270) osmotic pressure has been overlooked.

THE EFFECT OF SOIL CALCIUM ON THE MINERAL CONTENT OF WHEAT

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THE correction of soil acidity by calcium oxide or calcium carbonate often causes large increases in yield which are sometimes attributed as much to increases in the available calcium in the soil and in the calcium content of the crop as to a rise in the pH of the soil. The extent to which liming affects plant composition can be determined only by analysing plants from soils to which different dressings of lime have been applied.

A suitable site for this purpose was an area on the farm of the Hertfordshire Institute of Agriculture, Oaklands, St. Albans, which had been under experiment since 1934. The soil is a light to medium loam derived from Boulder Clay. Prior to 1933 it was woodland from which forest trees had been removed some years previously, leaving only scrub. The soil reaction was so low that in 1934 a 6×6 Latin Square experiment to determine manurial requirements showed a significant response of the potato crop to dressings of calcium carbonate (chalk) and an almost complete failure of the crop without applied phosphate. In 1934 a 5×5 Latin Square with varying levels of calcium carbonate (ground chalk) was also laid down on a different portion of the reclaimed land; this experiment has continued since, the area being treated in exactly the same way as the field of which it forms a part. The primary object of the trial was to relate field responses with the laboratory determination of lime requirement by the method of Hutchinson and McLennan. The lime requirement of the soil in 1934 was 75 cwt. of calcium carbonate per acre, and the rates of application chosen for the experiment were 0, $\frac{1}{2}$, 1, $1\frac{1}{2}$, and 2 times this figure. No further lime has been applied.

In August 1945 soil samples were taken from each of the 25 plots and were analysed by the Hellige-Truog method. There were practically no variations in the available phosphate, which was very low on every plot (about 0·2 mg. P_2O_5 per 100 g. soil). The exchangeable potash varied rather more, but there was no significant correlation with treatment and the mean value was 12 mg. K_2O per 100 g. soil. However, the treatments had caused large changes in the amount of lime extracted by 1 minute's shaking with 0·3 NHCl (Hellige–Truog reagent) and in soil pH (Table 1).

Although this acid extraction method extracts nearly all the calcium from soils, it seems likely that the figures in Table 1 represent mainly exchangeable calcium. Every application of chalk caused significant increases in readily soluble lime and in soil pH.

TABLE 1

Effect of Calcium Carbonate in 1934 on Soil Analyses in 1945 (Means of five plots)

Treatment cwt. ground chalk per acre	*Readily soluble* CaO, *mg. per 100 g. soil*	*Soil pH*
0	52	4·3
38	88	4·7
75	124	5·3
112	172	5·8
150	284	6·5
S.E.	±13	±0·12

In October 1945 the experiment was sown with Steadfast wheat, and therefore in 1946 it offered a good opportunity to study the effects of lime applied 12 years before on the nutrient contents of this crop. On five different occasions during the summer of 1946 plant samples were taken by cutting off tillers in alternate rows along the diagonals of each plot. The per cent. dry matter and dry weight per hundred tillers were determined on samples from individual plots, and these samples were analysed by the Lundegårdh flame method of spectrographic analysis for potassium, calcium, magnesium, and manganese.

For each sampling date Table 2 gives the mean values for the whole experiment and the average effect of unit dressing of chalk (38 cwt. per acre) calculated from the linear regressions of the values on the amounts of chalk originally applied. The tests of significance of these regression coefficients are based on the 12 degrees of freedom for error from analyses on all plots in the Latin Square.

TABLE 2

Effect of Calcium Carbonate on Plant Size and on Nutrient Concentration during Growth

	Mean of all plots					*Mean effect of unit chalk* (38 *cwt. per acre*)				
	g. dry matter per 100 tillers	*Concentration in dry matter*				*g. dry matter per 100 tillers*	*Concentration in dry matter*			
		% K	% Ca	% Mg	*p.p.m.* Mn		% K	% Ca	% Mg	*p.p.m.* Mn
Stems										
11 May	..	2·82	0·306	0·066	178	..	0·11‡	−0·001	0·005†	−53†
11 June	103	2·17	0·163	0·059	139	13†	0·02	0·003	0·006†	−44†
2 July	154	1·37	0·119	0·042	128	14	0·02	−0·002	0·006†	−35†
18 July	144	1·04	0·122	0·041	140	18	0·01	0·002	0·007†	−42†
15 August	116	0·60	0·129	0·031	140	13†	−0·02	0·002	0·004‡	−38†
Ears										
2 July	29	0·93	0·075	0·104	61	2	−0·005	−0·001	0·004	−9†
18 July	72	0·56	0·050	0·091	77	11‡	−0·002	−0·004	0·005	−21†
15 August	134	0·36	0·031	0·071	79	20	0·000	−0·003	0·002	−20†
Grain										
15 August	48·4•	0·35	0·028	0·101	56	9•	−0·002	−0·001	0·000	−4·5†

• Weight of 1,000 grain (g.). † *P* less than 0·01. ‡ *P* less than 0·05.

Dry Weight of 100 Tillers

The treatments had a highly significant effect on plant weight at every sampling time. On three occasions the increases in dry weight of the stems caused by an application of 75 cwt. of chalk per acre were highly significant (P less than 0·01). The effect on ear size was as strongly marked and the treatments even affected the weight of 1,000 grain, the first 75 cwt. of chalk per acre giving a highly significant increase in average grain weight, although the further dressings of lime gave smaller increases. These increases in stem, ear, and grain weights with increasing amounts of chalk were reflected in the yields at harvest.

Cwt. chalk per acre	*Yield of grain cwt. per acre*	*Yield of straw cwt. per acre*
0	3·2	18·9
38	8·7	24·1
75	13·2	28·6
112	15·2	29·7
150	15·8	30·3

Effect of Liming on Nutrient Concentration in the Dry Matter

Potassium. At the first sampling on 11 May the percentage of potassium was significantly increased by the liming; at the next three samplings the differences were small and not significant. At the final sampling on 15 August a significant decrease in the potassium concentration in the stems was caused by an application of 75 cwt. of chalk per acre, but there was no effect in the ears or in the harvested grain.

Calcium. The average effect of 38 cwt. of chalk per acre did not, on any occasion, cause a significant change in the calcium concentration in the dry matter. On one occasion, 18 July, the calcium concentration in the stems from the nil plot was significantly lower than in the stems from the limed plots. The only other significant effects were decreases in the calcium concentration in the ears with liming on 18 July and 15 August. In the harvested grain the calcium concentration was 0·030 per cent. on the nil plots and 0·027 per cent. on the most heavily limed plots, a difference below the 5 per cent. level of significance.

Magnesium. At the first sampling on 11 May the percentage magnesium was highly significantly increased by each additional dressing of chalk. At the next three samplings the chalk dressings as a whole caused highly significant increases in the magnesium concentration, but the individual dressings of chalk did not always cause significant increases. At the last sampling it required 112 cwt. of chalk to give a highly significant increase in the concentration of magnesium in the stems, although the average effect was just significant. The treatments increased the magnesium concentration in the ears to a smaller extent, although 150 cwt. of chalk per acre always gave a significant increase. The treatments had no effect on the concentration of magnesium in the harvested grain.

Manganese. On every occasion the treatments had a highly significant effect on the manganese concentration in both stems and ears. In every

case the lowest dressing of chalk decreased the concentration of manganese significantly, but generally a further significant reduction in the manganese concentration was obtained only by an additional 75 cwt. of chalk per acre. Even in the harvested grain 75 cwt. of chalk per acre had a significant effect on the manganese concentration. The highest manganese concentrations were in the first samplings, the p.p.m. ranging from 300 on the nil plots to 105 on the most heavily limed plots. At the final sampling the values ranged from 248 to 77 in the stems and from 133 to 47 in the ears. In the threshed grain the range was from 60 to 43. An analysis of the grain of the same variety of wheat grown on a neutral soil on the same farm had a manganese content of 24 p.p.m. It is clear therefore that although the manganese in the grain from the most heavily limed plot was still well above normal, liming had reduced the manganese contents towards more normal values.

Effect of Treatments on the Total Uptake of Nutrients

The total uptakes of nutrients by 100 tillers are given in Table 3 together with the uptakes at harvest expressed as lb. per acre.

Potassium. The treatments always increased the uptake of potassium. This was a result of increased plant size, since liming hardly affected the concentration of potassium in the plant. The total potassium content increased to a maximum, and by harvest had fallen to about half the maximum. In this case the maximum appeared to occur at the beginning of July and the time of occurrence was not affected by the treatments. Similar early maxima have been found by other workers (Knowles and Watkin, 1931; Remy, 1938; Woodford and McCalla, 1936).

Magnesium. The treatments very greatly increased the uptake of magnesium, since liming increased both plant size and the concentration of magnesium in the plant. The uptake of magnesium continued throughout the season on all plots, but was more rapid in early summer and fell off towards harvest.

Calcium. Although the treatments had little effect on the concentration of calcium in the plant they increased the total uptake by increasing the size of the plant. The uptake of calcium reached a maximum and then declined towards harvest, but the maximum for calcium was not nearly so pronounced and occurred rather later than that for potassium. This net loss of calcium from the plant at all levels of soil calcium indicates that even on the most acutely acid plots there was sufficient available calcium to satisfy the essential requirements of the crop.

Manganese. The treatments not only reduced the manganese concentration in the plant but also reduced the total manganese uptake. The manganese uptake continued throughout the season, the rate of uptake decreasing as the plant matured.

General Discussion

The increases in magnesium concentration resulting from the treatments suggest that the chalk used might have contained magnesium. A sample of chalk from the same pit contained 0·24 per cent. MgO and

TABLE 3

Effect of Liming on Total Content of Nutrients

Cwt. ground chalk per acre	*11 June*	*2 July*	*18 July*	*15 August*	*Harvested crop grain+straw*
	g. dry matter per 100 tillers				*Yield (cwt./acre)*
0 . .	75	153	138	167	22·1
38 . .	90	168	197	236	32·8
75 . .	103	184	238	253	41·8
112 . .	126	201	248	296	44·9
150 . .	122	217	257	300	46·1
	g. K *per 100 tillers*				*lb.* K *per acre*
0 . .	1·61	1·67	1·71	0·84	14·6
38 . .	1·94	2·20	1·17	1·16	20·8
75 . .	2·19	2·48	2·11	1·15	23·4
112 . .	2·77	2·72	2·26	1·34	25·4
150 . .	2·71	2·76	2·20	1·34	24·9
	g. Ca *per 100 tillers*				*lb.* Ca *per acre*
0 . .	0·11	0·18	0·13	0·12	2·6
38 . .	0·16	0·20	0·20	0·19	3·8
75 . .	0·17	0·20	0·24	0·19	4·7
112 . .	0·19	0·21	0·25	0·21	4·8
150 . .	0·21	0·24	0·24	0·22	4·9
	g. Mg *per 100 tillers*				*lb.* Mg *per acre*
0 . .	0·04	0·07	0·07	0·08	0·9
38 . .	0·05	0·08	0·09	0·10	1·5
75 . .	0·06	0·09	0·13	0·14	2·5
112 . .	0·08	0·11	0·16	0·16	3·0
150 . .	0·08	0·14	0·18	0·18	3·0
	g. Mn *per 100 tillers*				*lb.* Mn *per acre*
0 . .	0·020	0·031	0·031	0·032	0·55
38 . .	0·010	0·022	0·024	0·026	0·54
75 . .	0·012	0·020	0·025	0·026	0·51
112 . .	0·012	0·018	0·021	0·023	0·43
150 . .	0·009	0·015	0·016	0·018	0·34

therefore the dressings of chalk added 0, 10, 20, 30, and 40 lb. of MgO per acre. It is improbable that such small dressings could have any large effect 12 years later. It is likely that the availability of magnesium in the soil was increased by liming.

The most marked effect of liming on the composition of the wheat plant was the reduction in the concentration of manganese. 150 cwt. ground chalk per acre reduced the manganese concentration in the plant by about 66 per cent. This effect is probably due to the reduced availability of soil manganese at higher soil pH values, as has been shown by other workers (Jacks and Scherbatoff, 1940; Emmert, 1931).

One of the most striking results of the present investigation is the smallness of the effect of liming on the calcium concentration in the

wheat plant in spite of the decreased acidity and the increased exchangeable calcium in the soil. The 'available lime' as measured by the Hellige–Truog method was increased by the heaviest rate of liming from about 40 mg. per cent. to about 330, but the mean calcium content of the crop at harvest was reduced from 1·04 to 0·93 per cent. It has often been assumed that one of the benefits of liming is to improve the nutritive value of a crop by increasing its percentage of calcium, as distinct from merely increasing its size. This assumption is shown to be erroneous for wheat. That other crops probably behave in the same way as wheat is shown in Table 4 by some analyses carried out on crops grown on the same Latin Square in 1945. In this year different crops were sown along each of the rows of the square, and the effects of each of the treatments on five different crops were obtained.

TABLE 4

Composition of Crop Sample taken 14 May 1945

	Concentration in dry matter (mean of five plots)				*Effect of 38 cwt. of chalk per acre (half lime requirement)*			
Crop	% K	% Ca	% Mg	*p.p.m.* Mn	% K	% Ca	% Mg	*p.p.m.* Mn
Wheat	4·85	0·14	0·50	134	−0·05	0·01	0·02	−13
Oats	5·60	0·13	0·37	256	0·08	0·01	0·03	−94
Barley	3·96	0·14	0·46	132	0·53	0·00	0·00	−57
Peas	3·56	0·25	1·24	471	0·13	−0·03	−0·06	−294
Beans*	3·62	0·23	1·04	178	0·42	−0·01	−0·12	−87

* Crop failed completely without lime. Figures based on four plots only.

With mixed crops such as leys any increase in the calcium content of the herbage will depend mainly on the proportions of the different species, calcium increasing with the amount of legumes. This is illustrated in Table 5 by results obtained in 1947 when the same Latin Square was sown with rye grass and clover. When this was first cut for hay (13 June) samples were taken from each of the 25 plots. The mixed herbage from individual plots was analysed and bulked samples representing each of the five treatments were separated into their botanical constituents, which were also analysed.

These results indicate that the conclusions drawn for wheat are in the main valid for a much wider range of crops. There can be no doubt that the very high concentration of manganese in the plant at low soil pH is injurious, and that this is undoubtedly one reason for the reduced plant growth on acid soils. On liming such soils plant growth will be stimulated not only by the increased supply of calcium but also by the reduction in the adverse conditions associated with soil acidity.

The very small effect of liming on the calcium content of the crop does not necessarily mean that the increased supply of calcium is without effect on plant growth. Goodall and Gregory (1947) point out that as the supply of a nutrient is increased from very low levels plant growth is increased, but the concentration of the nutrient in the dry matter

TABLE 5

Effect of Liming on the Nutrient Content of Mixed Herbage and of Some Separated Botanical Species

	Concentration in dry matter Mean of five treatments				*Effect of 38 cwt. chalk per acre (half lime requirement)*			
	% K	% Ca	% Mg	*p.p.m.* Mn	% K	% Ca	% Mg	*p.p.m.* Mn
Mixed herbage	1·99	0·21	0·10	236	−0·062	0·008	0·018	−31
Clover	2·08	1·17	0·18	108	−0·025	−0·095	−0·004	−11
Rye grass	1·85	0·20	0·10	170	−0·039	−0·004	−0·002	−14
Holcus lanatus	2·63	0·22	0·14	258	−0·061	−0·004	−0·002	−14
Other grasses	2·52	0·21	0·14	326	−0·163	−0·013	−0·003	−45
Sorrel	1·74	0·23	0·13	378	−0·065	−0·002	0·002	−62
Weeds	2·04	0·52	0·19	102	0·154	0·013	0·009	−19

decreases to a minimum and then increases, until at high levels of supply, 'luxury uptake' occurs. The results of the present paper show that over a range of soil pH values between 4·3 and 6·5 the calcium percentage in wheat and other crops is in the region where it is little influenced by liming. The very wide range of readily soluble soil calcium which is associated with these changes in soil pH does not appear to include the conditions either of 'luxury uptake' or of 'deficiency'. It seems probable that the range over which concentration is unaffected by supply is extended in the case of calcium because at low levels of calcium supply there are other factors resulting from the acidity of the soil which also limit plant growth. In the practically important case of leys and other mixed fodder crops the effect of liming in increasing the calcium content of the fodder is to be ascribed mainly to the increased proportion of leguminous plants.

While the results of the present paper apply to one soil only, it seems probable that liming may give similar results on other acid soils, although not necessarily over the same soil pH range.

Summary

A Latin Square experiment put down 15 years ago to test the value of the Hutchinson and McLennan determination of lime requirement was used to determine the long-term effect of liming on the uptake of nutrients by the plant. The site was sown with Steadfast Wheat in 1946 and samples were taken on five occasions. The main changes with liming were increased plant size, decreased concentrations and total contents of manganese in the plant, and increased concentrations and total contents of magnesium in the plant. Calcium and potassium concentration were almost unaffected by the treatments, although the total content in the plant was increased through increased plant size.

Analyses of other crops grown on the same site in 1945 and 1947 indicate that these effects are not specific for wheat, and especially that

the increased calcium concentration in mixed herbage resulting from liming is due to a higher proportion of legumes.

The effect of liming on yield is attributed to the reduction in soil acidity and to the increased supply of calcium. The reduced soil acidity is reflected in reduced uptake of manganese by the plant, but the increased supply of calcium is compensated by increased plant growth.

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FIXATION OF PHOSPHATE DURING THE ACID EXTRACTION OF SOILS

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Introduction

FOR many years chemists have estimated the amounts of phosphate present in soils that are likely to serve as plant nutrient, but correlation of the amounts of phosphate extracted by dilute acids from soils with the amounts taken up by crops has not been highly successful. Discrepancies are due to two main causes. The first is inherent in dilute acid extraction, which was originally based on the idea that plants dissolve plant nutrients through the acids their roots exude. This mechanism of plant feeding is no longer fully supported. Ionic exchanges between the soil and the plant root may result in the uptake of ions not dissolved in dilute acid extraction. The second cause of discrepancy depends on the fact that the acid solution has a much lower pH value than most field soils. Phosphates not normally available as plant food are dissolved, and the phosphate dissolved may undergo secondary reactions, some being precipitated by bases present in the extract or by the soil colloids in contact with the extractant. Precipitation of phosphate from solution to forms which are useless to plants or are insoluble in the conventional acid extractants is commonly termed 'fixation'. The problem of phosphate fixation during the acid extraction of soils has been investigated in the present work.

Three mechanisms of phosphate fixation in acid soils are usually postulated. (1) Chemical precipitation by soluble salts of iron, aluminium, titanium, and manganese. (2) Adsorption by the hydrous oxides of iron, aluminium, titanium, and manganese. (3) Adsorption by aluminosilicates. Critical reviews of the extensive literature on phosphate fixation have been given by Midgely (1940) and by Wild (1950).

When a soil is extracted with dilute acid all the three types of fixation described may occur, the last two probably being the most important. Tentative methods have been proposed to measure the amount of acid-soluble phosphate in the absence of fixation. Burd and Murphy (1939) state that satisfactory correlations with crop growth are obtained if, together with the acid-extractable phosphate, the degree of phosphate saturation of the adsorbing minerals, the buffer capacity, and the total phosphate content of the soil are taken into account. Kurtz, De Turk, and Bray (1946) studied the ability of a number of anions to 'replace' phosphate from soils and found the order of 'replacing ability' to be fluoride > oxalate > citrate > bicarbonate > borate > acetate > thiocyanate > sulphate > chloride. Bray and Dickman (1941) proposed a method for fractionating inorganic soil phosphates based on the replacement of 'adsorbed' soil phosphates by fluoride solutions. Swenson, Cole, and Sieling (1949) found that arsenate and fluoride replaced

chemically combined phosphate and that organic ions such as citrate and tartrate had the same property. Humus and lignin replaced phosphate from basic iron phosphates.

Experimental

Analytical methods

All phosphate determinations were made by the method of Truog and Meyer (1929).

It was necessary to remove selenium since a red precipitate appeared on adding stannous chloride during the phosphate determination. The liquid was evaporated to a small bulk and 20 ml. of concentrated hydrochloric acid were added. Sulphur dioxide was passed into the liquid for 1 hour. The selenium precipitated was filtered off and the filtrate evaporated to 2 ml. This process did not remove the last trace of selenium. 20 ml. of water were added followed by 1 ml. of ammonium sulphide (free from arsenic and phosphorus). Sufficient dilute hydrochloric acid was added to make the liquid acid and the flask was corked lightly and allowed to stand to coagulate precipitated sulphur. The liquid was filtered and the filtrate was evaporated to dryness with the addition of 2 drops of concentrated nitric acid to oxidize colloidal sulphur. The residue was dissolved in dilute hydrochloric acid and phosphate was determined on an aliquot after neutralizing.

Organic matter was removed from soil extracts when necessary by ashing with calcium acetate or magnesium nitrate.

Phosphate fixation by metallic oxides in acid suspension

The common oxides occurring in soils which are likely to precipitate phosphate in acid solution are those of titanium, iron, aluminium, and manganese. Samples of these oxides were prepared. The fixation of phosphate by a suspension of oxide in 0·5N acetic acid was determined in the presence and absence of a number of reagents which were known to form insoluble compounds or absorption complexes with the metal concerned.

Materials used

TiO_2 I. Potassium titanium oxalate was heated with concentrated H_2SO_4 to destroy oxalate. Titania was precipitated by NH_4OH and was washed until free from impurities. The preparation was air-dried and ground.

TiO_2 II. TiO_2 I was ignited at 280–300° C. for 2 hours and was then finely ground.

Fe_2O_3 was prepared by precipitation from ferric ammonium sulphate with NH_4OH. It was washed and then dried to constant weight at 55–60° C. The preparation had the approximate composition Fe_2O_3, $3H_2O$.

Al_2O_3 I was precipitated from aluminium sulphate solution by excess NH_4OH and washed until the washings were free from sulphate. This preparation contained a small amount of sulphate as was shown by

treating it with oxalate solution. The material was air-dried and ground.

Al_2O_3 II. Al_2O_3 I was ignited at 300° C.

Al_2O_3 III. A slight excess of $BaCl_2$ was added to potash-alum solution. H_2SO_4 was added slowly until a drop of the supernatant liquid gave no colour with sodium rhodizonate. $BaSO_4$ was filtered off and alumina was precipitated by excess NH_4OH. The preparation was washed until free from ammonium and chloride and then dried over conc. H_2SO_4 *in vacuo*.

Al_2O_3 IV was a commercial preparation supplied by Merck for use in chromatographic analysis.

MnO_2. A slight excess of NaOH was added to $MnSO_4$ solution. The precipitate was washed until the washings were free from sulphate and were neutral. It was dialized against distilled water in a collodion sac and dried over conc. H_2SO_4. The preparation became black and probably consisted of a mixture of manganese hydroxides and oxides.

A lateritic soil (No. 1608) from Sierra Leone was used which probably contained much free sesquioxides.

Experimental method

All the experiments on phosphate fixation were made with a solution of the reagent in 0·5N acetic acid; when necessary the pH of the solution was adjusted to 2·5 by adding HCl or NH_4OH. A suspension of oxide was shaken for 2 hours with the reagent dissolved in 195 ml. of 0·5N acetic acid. Then 5 ml. of KH_2PO_4 solution was added containing 0·1 mg. P_2O_5 per ml. The suspension was shaken for a further 2 hours, filtered, and the phosphate remaining in solution was determined. Filtration of suspensions containing alumina was difficult and slow. A membrane filter was used and the equilibrium between phosphate and oxide was liable to alter during filtration. The results of the experiments are given in Table 1.

Although 8-hydroxyquinoline forms insoluble complexes with titanium and aluminium, it reduced phosphate fixation by the oxides only slightly. Citrate and oxalate prevented most of the fixation by ferric oxide and alumina, but both ions tended to dissolve ferric oxide. Fixation of phosphate during acid extraction of soils should be reduced if citric acid is used as solvent. Morin and quinalizarin, which form complexes with aluminium, prevented a great part of the fixation caused by alumina. Ferrocyanide reduced fixation by alumina, which accords with the position of the ion in the table of absorption affinities for alumina given by Zechmeister and Cholnoky (1938). Fluoride reduced phosphate fixation by alumina markedly. Bray and Dickman (1941) have used fluoride solutions to measure the 'replaceable' phosphate in soils.

Selenious acid was the most satisfactory reagent. A 0·5 per cent. solution in 0·5N acetic acid reduced fixation by all three oxides from nearly 100 per cent. to very low values. The manganese-oxide preparation fixed rather small amounts of phosphate; fixation was partially prevented by selenious acid. The lateritic soil fixed most of the phosphate added, but the greater part of the fixation was prevented by selenious acid.

TABLE I

The Value of Reagents in preventing Phosphate Fixation by Hydrous Oxides in Acid Suspension

Oxide	*Amount (g.)*	*Reagent*	*Amount (g.)*	*Percentage fixation of added phosphate*	
				Without reagent	*With reagent*
TiO_2 I . .	0·100	8 (OH) quinoline	0·75	96	74
TiO_2 II . .	0·025	Selenious acid	0·25	93	5
TiO_2 II . .	0·025	Selenious acid	0·50	93	3
Fe_2O_3 . .	0·050	8 (OH) quinoline	0·50	100	86
Fe_2O_3 . .	0·050	8 (OH) quinoline	1·00	100	74
Fe_2O_3 . .	0·050	Citric acid	1·00	100	12
Fe_2O_3 . .	0·050	Selenious acid	0·25	100	18
Fe_2O_3 . .	0·050	Selenious acid	0·50	100	9
Fe_2O_3 . .	0·050	Selenious acid	1·00	100	3
Al_2O_3 I . .	0·200	8 (OH) quinoline	1·00	63	47
Al_2O_3 II . .	0·030	Morin (in alcohol)*	1·00	90	29
Al_2O_3 II . .	0·030	Quinalizarin (in alcohol)*	1·00	80	36
Al_2O_3 II . .	0·030	Citric acid	1·00	68	11
Al_2O_3 II . .	0·030	Oxalic acid	1·00	68	14
Al_2O_3 II . .	0·030	Ammonium fluoride	1·00	71	12
Al_2O_3 II . .	0·030	Potassium ferrocyanide	1·00	68	27
Al_2O_3 III .	0·100	Selenious acid	1·00	85	5
Al_2O_3 IV .	0·050	Selenious acid	1·00	62	6
MnO_2 . .	0·100	Selenious acid	1·00	35	18
Lateritic soil .	0·500	Selenious acid	2·50	84	33
Lateritic soil† .	0·500	Selenious acid	2·50	84	24

* These reagents were dissolved in the minimum quantity of alcohol. The alcoholic solution was added to sufficient 0·5N acetic acid to give a total volume of 195 ml.

† The soil was treated with selenious acid for 48 hours in this experiment.

Phosphate fixation by clay minerals in acid suspensions

Murphy (1939) found that kaolin fixed considerable amounts of phosphate between pH 4 and pH 8; fixation was greatest at the lower pH and was increased by grinding the kaolin in a ball mill. Sieling (1946) stated that acid-washed kaolin does not absorb phosphate, but that, if it is ball-milled, kaolin absorbs phosphate to an extent depending on the duration of the milling. The active constituent of ball-milled kaolin was believed to be a hydrous alumina. Coleman (1944) concluded that little or no phosphate is fixed by pure montmorillonite and kaolinite, but that phosphate is fixed by free iron and aluminium oxides present in these minerals.

The clay minerals used in this study were commercial kaolin, Missouri halloysite (ground in an agate mortar), and bentonite.

0·2 g. of mineral was shaken for 2 hours with 195 ml. of 0·5N acetic acid containing 1·25 per cent. selenious acid and adjusted to pH 2·5. 0·5 mg. of P_2O_5 was added (as 5 ml. of a solution of KH_2PO_4) and shaking was continued for a further 2 hours. Determinations were made of the amount of phosphate extracted from the minerals alone and of the extent

of the fixation which occurred in the absence of selenious acid. Similar experiments on kaolin and halloysite were made at pH 4·5 using NH_4OH to partially neutralize acetic acid and the mixture of acetic and selenious acids. The results of the experiments on clay minerals are given in Table 2.

TABLE 2

The Effect of Selenious Acid on Fixation of Phosphate by Clay Minerals in Acid Suspensions

Mineral	*Percentage fixation of added phosphate*	
	Without selenious acid	*With selenious acid*
Experiments at pH 2·5		
Kaolin . . .	2·6	4·5
Halloysite . . .	7·6	7·8
Bentonite . . .	18·0	18·6
Experiments at pH 4·5		
Kaolin . . .	2·8	7·0
Halloysite . . .	3·8	10·6

Kaolin and halloysite did not fix appreciable amounts of phosphate at pH 2·5 or 4·5. Selenious acid extracted more phosphate from the minerals and caused small increases in the amount of fixation at both pH values. Bentonite fixed appreciable amounts of phosphate at pH 2·5 and fixation was not reduced by selenious acid.

Effect of varying amounts of selenious acid on the phosphate extracted from soils

Preliminary experiments showed that mixtures of selenious and acetic acids at pH 2·5 extracted more phosphate from soils than acetic acid alone. This may be due in part to immediate fixation of phosphate dissolved by the acetic acid when selenious acid was absent. Acids used to extract soils should not dissolve compounds which are useless to crops; citric acid is thought to dissolve iron phosphates from some soils and give misleadingly high values for 'available' phosphate. Varying amounts of selenious acid were used to extract soil and determine whether a constant fraction of the soil phosphate was dissolved. A laterite from Kenya (4945) and a sandy soil derived from Triassic materials from Oxton, Nottinghamshire (S1938), were chosen for these experiments. 0·5 g. of each soil was shaken for 2 hours with 200 ml. of 0·5N acetic acid containing various quantities of selenious acid. The pH of the acid mixture was adjusted to 2·5. The results of the extractions are given in Table 3.

The two soils behaved similarly on extraction with selenious acid. Acetic-selenious acid mixture extracted more phosphate than acetic acid alone. With both soils there was a wide range where the extracted

TABLE 3

Effect of Varying Concentrations of Selenious Acid on the Phosphate Extracted from Soils

Soil 4945		*Soil S1938*	
Selenious acid used (g.)	P_2O_5 *extracted (mg. per 100 g.)*	*Selenious acid used (g.)*	P_2O_5 *extracted (mg. per 100 g.)*
0·0	0·0	0·0	8·0
0·75	14·6	0·05	12·6
1·5	13·4	0·1	13·9
2·5	15·0	0·25	15·2
5·0	17·0	0·5	15·8
10·0	30·6	1·0	16·2
		2·0	17·8
		4·0	29·2
		8·0	50·0

phosphate increased only slowly as the selenious-acid concentration increased. Above a certain concentration the phosphate extracted rose rapidly, indicating that another fraction of soil phosphate was being dissolved.

Recovery of insoluble calcium phosphates from soils

In most soils calcium phosphates added as fertilizers undergo slow chemical reactions to form new compounds. The speed of these reactions and the nature and value of the compounds formed depend on the capacity of the soil to fix phosphates. Recent applications of phosphate fertilizer are dissolved by acid extraction, but if, during the extraction process, the dissolved phosphates are precipitated immediately by soil constituents, no trace of the fertilizer will be found. In some tropical soils recent applications of fertilizer cannot be detected by extracting with the usual dilute acids. Experiments were made using selenious acid to reduce or prevent fixation by laterite soils from Sierra Leone (1608) and from Kenya (4945). 10 g. of each soil were mixed with 20 mg. of pure dicalcium phosphate. A mixture of 10 g. of Sierra Leone laterite was also made with 20 mg. of Gafsa mineral phosphate (containing 25·7 per cent. P_2O_5). 0·5 g. samples of the soil-phosphate mixtures were extracted by shaking with 200 ml. of 0·5N acetic acid and with 0·5N acetic containing 1·25 per cent. of selenious acid (the pH of the mixture of acids was adjusted to 2·5) (Table 4).

Recovery of mineral phosphate from the Sierra Leone laterite was almost complete when selenious acid was present. The method was less successful for recovering dicalcium phosphate, presumably because this compound dissolved in the acid mixture more rapidly. The Kenya laterite fixed less than half of the dicalcium phosphate when extracted with acetic acid; recovery was almost complete when selenious acid was used.

TABLE 4

Extraction of Added Calcium Phosphates from Laterite Soils by Acetic and Selenious Acids

Soil No.	*Phosphate added*	*Percentage fixation of added phosphate*	
		Without selenious acid	*With selenious acid*
1608	$CaHPO_4$	92	26
1608	Mineral phosphate	92	9
4945	$CaHPO_4$	42	4

Extraction of soils with acetic-selenious acid mixtures

A series of 32 soil samples from fields where manuring experiments on sugar beet had been carried out in 1938 were extracted at pH 2·5 with 0·5N acetic acid containing 0·5 per cent. selenious acid. The phosphate dissolved by selenious-acetic acids did not give more satisfactory correlations with the responses of the sugar-beet crops to dressings of superphosphate than the phosphate dissolved by 0·5N acetic acid alone or by 1 per cent. citric acid (data are not presented here). The amounts of added phosphate fixed by these soils in 0·5N acetic acid were determined and found to be very small.

Selenious acid was used in an attempt to prevent fixation of added phosphate by six British soils which had a high capacity to fix phosphate. 0·5 g. of soil was shaken for 2 hours with 195 ml. of 0·5N acetic acid containing 0·5 per cent. of selenious acid. 5 ml. of KH_2PO_4 solution containing 0·1 mg. P_2O_5 per ml. was added and the suspension was shaken for a further 2 hours. After filtering, the phosphate remaining in solution was determined. The amount of added phosphate fixed in 0·5N acetic acid was also determined. The results of these experiments are given in Table 5.

TABLE 5

Phosphate fixed by British Soils in Acetic Acid and in a Mixture of Acetic and Selenious Acids

Soil		*Percentage fixation of added phosphate*	
		Without selenious acid	*With selenious acid*
2832	Ironstone	25	12
3328	Drift	33	24
3340	Lias	47	21
3599	Sandy fen	29	−7
4055	Clay fen	45	18
4341	Granite	21	20

Fixation by the sandy fen soil was prevented completely by selenious acid. The reagent had no effect on fixation by the granite soil but reduced fixation by the other soils to varying degrees.

Discussion

Suitable amounts of selenious acid dissolved in 0·5N acetic acid prevented fixation of added phosphate by hydrous oxides of titanium, iron, and aluminium. The reactions involved are difficult to assess. Iron and titanium selenites are insoluble at pH 2·5, but aluminium selenite is not readily precipitated. It is possible that selenite ions replace hydroxyl groups on the surface of the hydroxides. If the complexes are highly undissociated, phosphates will not be able to combine with the hydroxides. Mass-action effects must be important as the quantities of selenious acid used were very large in relation to the phosphate added to the oxide suspensions.

The preparations of clay minerals used fixed relatively small proportions of added phosphate at pH 2·5; the fixation which occurred was not reduced by selenious acid. In soils where aluminosilicate minerals of the types tested are responsible for fixation during acid extraction, selenious acid will not provide more satisfactory values for acid-soluble phosphate than acetic acid.

A series of thirty-two soils on which sugar-beet experiments had been carried out fixed very small proportions of added phosphate. Reprecipitation of phosphate during acid extraction was not responsible for such lack of correlation as existed between acid-soluble phosphate and responses of the crops to applications of superphosphate. A reagent which prevents fixation has no special merit for such soils.

In the six British soils which caused marked fixation in acetic-acid suspensions, selenious acid prevented fixation to a varying degree. As selenious acid did not reduce fixation by the granite soil (4341) hydrous oxides were not responsible for the precipitation of added phosphate. Presumably fixation by the sandy fen soil (3599), which was completely prevented by selenious acid, was caused solely by hydrous oxides. It may be postulated that fixation by the other four soils was caused partly by hydrous oxides and partly by other soil minerals.

For soils where fixation in acid extraction is caused largely by hydrous oxides, selenious-acetic acid mixtures will give a more satisfactory value for acid-soluble phosphate than acetic acid alone. The reagent is valuable in demonstrating the fate of added phosphate fertilizers in lateritic soils. As selenious acid had no effect on fixation caused by the clay minerals tested, it may be possible to distinguish between soils where fixation is mainly due to hydrous oxides and those where other soil constituents are responsible.

Summary

Preparations of the hydrous oxides of titanium, aluminium, and iron suspended in 0·5N acetic acid fixed considerable amounts of added phosphate. Tests were made to prevent fixation at pH 2·5 by dissolving reagents in the acetic acid. 8-hydroxyquinoline reduced fixation by each of the three oxides, and selenious acid prevented fixation completely. Citric acid prevented fixation by ferric oxide. Citrate, oxalate, fluoride, ferrocyanide, morin, and quinalizarin all reduced fixation by alumina.

Selenious acid prevented most of the phosphate fixation caused by a laterite soil at pH 2·5.

Kaolinite and halloysite fixed very small proportions of added phosphate at pH 2·5 and at pH 4·5. Bentonite fixed appreciable amounts of phosphate at pH 2·5. Selenious acid did not reduce fixation by any of these clay minerals.

Small amounts of the phosphate added as dicalcium phosphate and mineral phosphate were recovered when laterite soils were extracted with 0·5N acetic acid. Satisfactory amounts of the added phosphate were recovered when selenious acid was present in the extractant.

In a series of British soils from manuring experiments on sugar beet there was very little fixation of added phosphate during extraction at pH 2·5; there was no advantage from adding selenious acid to prevent fixation. Six other selected British soils fixed considerable amounts of added phosphate at pH 2·5. Selenious acid prevented varying proportions of the fixation caused by five of the soils and had no effect on fixation by the sixth soil.

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